

**ASSESSMENT OF PUBLIC HEALTH RISK OF HEAVY
METALS FROM CONTAMINATED WATER, SOIL AND
EDIBLE VEGETABLES IN SELECTED AREAS OF NASARAWA
STATE, NIGERIA**

BY

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ABSTRACT

This study assessed the public health risk of heavy metals from contaminated water, soil and edible vegetables in selected industrialized area of Lafia, Nasarawa State, North Central Nigeria. A total of ten (10) contaminated water, edible vegetables and soil samples were collected within different proximate locations of human anthropogenic activities in Lafia Local Government and analysed for the presence of heavy metals using standard methods. Four (4) varieties of edible vegetables namely: *Telfairia occidentalis*, *Amaranthus hybridus*, *Talinum Triangulare* and *Corchorus* sp. were investigated for the presence of heavy metals and soil-vegetable transfer coefficients. One hundred and twelve (112) human inhabitants living within the sampling locations were selected using simple random sampling technique and assessed for health risk employing the Inductively Coupled Plasma-Atomic Emission Spectrometry Instrument (ICP-AES) with axial viewing configuration. Seven (7) heavy metals were detected in all samples analysed. Among such includes Cd, Cu, Zn, Mn, Pb, Fe and Ni. The mean contamination degree was highest for Fe (106.02) and lowest for Pb (0.05). The Pollution Load Index of soil was >1 while those of water and edible vegetables were less than 1. The mean risk index of heavy metals on the environment was in the order: soil (77.11) > edible vegetables (69.67) > water (66.39). Exposure concentration of the heavy metals on the study population for soil (mg/kg) is in the range of 0.73–98.90 ppm while that of water (mg/ml) is between 1.00–233.31 ppm. Conversely, estimated daily intake showed varying results for the vegetables between the ranges of 0.001–0.034 mg/kg. The hazard index was highest for Fe (4.298) and lowest for Pb (0.418) and this followed the order: Fe > Zn > Cu > Ni > Mn > Cd > Pb. The soil-vegetable transfer coefficients showed an efficacy of 1.99 for *T. occidentalis*, 1.52 for *A. hybridus*, 1.25 for *Corchorus* sp. and 1.01 for *T. triangulare*. From the data obtained from this study, it was observed that no matter how low levels of heavy metals are present in environmental samples particularly in vegetables, their presence pose health risk and is thus not desirable. The presence of cadmium, copper and lead in the edible vegetables analysed is a cause for alarm and denote serious public health risk to consumers of this food. Therefore, there is need for regular scrutiny soil, irrigating water, and foodstuff for heavy metals so as to avoid extreme accrual in the food chain which may eventually elude human health risks. Consequently, this study encourages environmentalists, administrators, and public health workers to create public awareness to avoid the consumption of vegetables grown in contaminated soils, hence reducing health risks.

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

Heavy metals refer to metals with a specific gravity greater than five (5). They are toxic and accumulate within organisms in the natural environment (Enuneku *et al.*, 2018). They are ubiquitous in the environment and due to rapid urbanization and industrialization worldwide, it is anticipated that heavy metals are being continuously introduced into the environment from a variety of sources such as discharge of domestic sewage, industrial wastewater, discharge of urban and industrial solid wastes, exhaust pipes of motor cars, generators and chimneys, usage of agrochemicals and atmospheric deposition (Fosu-Mensah *et al.*, 2018). In the aquatic environment for instance, heavy metals can be discharged via several routes including effluent/waste discharge, run-offs, leachates, shipping activities, and atmospheric depositions, especially from industrial and urban areas (Maanan, 2008; Enuneku *et al.*, 2018). Environmental pollution due to heavy metals has harmful effects on both plants and animals (Förstner and Wittmann, 2012).

Heavy metals pollution in soil and water has a lot of adverse effects and thus is of great concern to public health and agricultural production. The soil pollution is mainly due to disposal of industrial and urban wastes as well as usage of agrochemicals, while water pollution is primarily caused by industrial wastes, sewage disposal, petroleum contamination, and agricultural drainage water (Singh *et al.*, 2010). Many growing developing countries are vulnerable to air pollution due to the fact that heavy metals containing aerosols are normally deposited on soil

surface and get absorbed by vegetables or sometimes get deposited on plant leaves (Sharma *et al.*, 2006). The uptake of heavy metals by the plants from the soil depends on different factors, including application of agrochemicals, solubility of heavy metals, soil pH, soil type, and plant species (Gupta *et al.*, 2013; Kacholi and Sahu, 2018).

In addition to causing environmental damage, heavy metals in soil, air, and other media in mining-affected areas enter plants by absorption through the vegetable roots and dust on leaves (Li *et al.*, 2017). Meanwhile, ingestion of heavy metals can upset the body chemistry, especially because these metals do not undergo decomposition within the body and have a high affinity for many body systems (Duruibe *et al.*, 2007). Increasing evidence indicates that oral exposure is the most important way for heavy metals in the environment to enter the body; contaminated soil can result in heavy metal translocation into the food chain, and high consumption of contaminated vegetables can pose a serious risk to the human body (Hough *et al.*, 2004; Yeganeh *et al.*, 2012). Interestingly, several studies such as those of Li *et al.* (2013), Ha *et al.* (2014) and Huang *et al.* (2016) of the accumulation and origin of heavy metals in soil and the potential ecological hazards associated with this process have revealed an increasing trend.

Recently, some intensive research has attracted attention to the effects of heavy metals on human health, especially in infants and children (Krishna and Mohan, 2016; Izhar *et al.*, 2016). Humans generally are exposed to toxic heavy metals in the environment through different routes including ingestion, inhalation, and dermal absorption. People are more exposed to toxic metals in developing countries (Kpan *et al.*, 2014). Generally, people have poor awareness and knowledge about exposure

to heavy metals and its consequences for human health, especially in the developing countries. People may be exposed to heavy metals in the work place and in the environment (Noli and Tsamos, 2016). Human exposure to toxic chemicals in the work place is called occupational exposure while exposure to such chemicals in the general environment is called non-occupational or environmental exposure. Workers are exposed to heavy metals in mining and industrial operations where they may inhale dust and particulate matter-containing metal particles. People extracting gold through the amalgamation process are exposed to mercury (Hg) vapours (Ali *et al.*, 2019).

Also, it has been reported that welders with occupational prolonged exposure to welding fumes had significantly higher levels of the heavy metals chromium (Cr), nickel (Ni), cadmium (Cd), and lead (Pb) in blood than the control and showed increased oxidative stress (Mahmood *et al.*, 2015). Cigarette smoking is also a principal source of human exposure to Cd and other toxic heavy metals present in the tobacco leaves (Järup, 2003). On the other hand, heavy metals may enter the body of an organism directly from the abiotic environment, i.e., water, sediments, and soil or may enter the organism body from its food/prey. Ali *et al.* (2019) reports further that heavy metals are strong neurotoxins in fish species. The interaction of heavy metals with chemical stimuli in fish may interrupt the communication of fish with their environment.

Among many toxic elements, lead, arsenic, and cadmium are considered to be potential carcinogens and are associated with the development of several diseases, especially cardiovascular, kidney, nervous system, blood, and bone diseases (Järup, 2003). Although copper is an essential element for humans, a high concentration in

soil and vegetables leads to human toxicity (Yang *et al.*, 2018). Acute exposure to heavy metals in the environment is a threat to living organisms (Wieczorek-Dabrowska *et al.*, 2013). For instance, high zinc content may cause growth and reproduction impairment; while lead toxicity causes dysfunction of kidney, reproductive, cardiovascular systems, joints problems, lessening in haemoglobin formation, and enduring impairment to the central and peripheral nervous systems (Tasrina *et al.*, 2015).

Consequently, this present study sought to assess the public health risk of heavy metals in contaminated water, soil and edible vegetables in some selected industrialized areas of Nasarawa State, North-Central Nigeria. It is plausible to add that monitoring and analysis of heavy metal concentrations in the physical environment are imperative for pollution assessment and control. Hence, data obtained from this present research will assist government and other relevant agencies to take appropriate remediation approach that will protect the health of the inhabitants of the study areas in particular and the wellbeing of the environment in general.

1.2 Statement of the Problem

The study area (Nasarawa State) is nicknamed “The Home of Solid Minerals”, and mining activities at both local and industrial scale is pervasive. Yang and colleagues (2018) in their research on heavy metal contamination of soils and vegetables in China noted that the smelting process in metal mines can produce large amounts of waste, resulting in high accumulation of heavy metals in the soil and in the river and underground water surrounding the mining area. This connotes public health risk considering the role of the environment in the transmission of diseases within a

population and the fact that most of these heavy metals are carcinogenic. Even so, Kacholi and Sahu (2018) described heavy metals pollution as a menace to our environment as they are foremost contaminating agents of our food supply.

In response to the growing public concern about heavy metal pollution, there has been an increase in the monitoring of heavy metal concentrations in both aquatic and terrestrial systems globally. More so, the presence of toxic levels of heavy metals in benthic organisms has led to a sharp reduction in the diversity, growth, and reproduction rates of these organisms (Massaquoi *et al.*, 2015). In addition, contamination of the soil ecosystem by heavy metals is a critical environmental challenge because the metals persist in the environment (Pakade *et al.*, 2012; Babatunde *et al.*, 2014); as such, soil is a major source of contamination to the food web and this makes it a preferred indicator for assessment of heavy metal contaminations (Ra *et al.*, 2013).

For instance, 160–392 $\mu\text{g/g}$ of Zn was detected in soil samples in Uyo, South South Nigeria by Odousoro *et al.* (2010). The concentration of Ni and Zn in plant in different sites around Malete, Kwara State, North Central part of Nigeria varied between 1.65–1.85 mg/kg and 23.9–117.8 mg/kg respectively as reported by Ogundele and colleagues (2015). In Lagos, South Western Nigeria on the other hand, specific emissions of Pb exceed 164 kg/km^2 , representing approximately 20% of the 2.46Gg of Pb emissions nationwide (Orisakwe *et al.*, 2014). Hence, the potential health consequences of heavy metal toxicity on humans through food and water ingestion are an issue of serious public health concern in Nasarawa State in particular and Nigeria in general.

1.3 Justification of the Study

In Nigeria, several studies have determined the presence of heavy metals in various environmental compartments and biota. Nasarawa State is noted for its massive agricultural and mining activities that have led to increased rate of heavy metal contamination and pollution. At present, assessment and monitoring of heavy metal contamination in the state has been predominately based on chemical analysis of environmental compartments of water, sediment, and soil alone. This step is fundamentally insufficient in deriving the potential toxicity of contaminated environmental samples. Moreover, chemical analysis on abiotic compartments cannot directly assess the antagonistic or synergistic effects as well as the bioavailability of toxicants to organisms because the magnitude of contamination does not necessarily reflect a similar level of eco-toxicological effect as observed by Barhoumi *et al.* (2016).

Air, water, and soil are the most important components of the living environment for human beings. In recent years, with the quick development of urbanization and industrialization, the contamination of soil by heavy metals has become an increasing public health concern (Sun, 2017). This present study nonetheless sought to investigate the ecological as well as the public health risk of heavy metals contamination in water, soil and edible vegetables in some selected areas of Nasarawa State. Thus awareness will be created about the preponderance of heavy metals in this environmental samples and the threat they pose to people and communities inhabiting such areas.

1.4 Research Questions

This research attempts to answer the following questions:

- i. What are the heavy metals and their concentration present in water, soil and edible vegetables in selected exposed areas?
- ii. What natural or artificial activities (e.g. mining, agriculture, industrial works, etc.) across human population that could expose individuals to heavy metals in the environment?
- iii. What are the short and long term public health risks or impacts of exposure to heavy metals among the inhabitants of the areas sampled?

1.5 Research Aim and Objectives

1.5.1 Aim of the Research

This study aimed at assessment of public health risk exposure of heavy metals in contaminated water, soil and edible vegetables in some selected areas of Lafia, Nasarawa State, Nigeria.

1.5.2 Objectives of the Research

The specific objectives of the study include;

- i. To determine the types of heavy metals present in the study areas.
- ii. To analyse the level or concentration of the heavy metals in contaminated water, soil and edible vegetables in the study area.
- iii. To assess the ecological impacts of the heavy metals on the environment.
- iv. To evaluate human health impact assessment at various locations contaminated by natural or artificial activities.

1.6 Research Hypotheses

The following hypothesis was tested at level of significance at 0.05.

1.6.1 Null Hypothesis (H₀)

There is no effect or relationship between heavy metal concentrations in contaminated water, soil, edible vegetables and health risk or status of people in the selected areas.

1.6.2 Alternate Hypothesis (H₁)

There is an effect or relationship between heavy metal concentrations in contaminated water, soil, edible vegetables and health risk or status of people in the selected areas.

1.7 Scope of the Research

This present study was restricted to the assessment of heavy metals in contaminated water, soil and edible vegetables across proximate residential–industrial areas of Lafia Local Government of Nasarawa State, Nigeria.

1.8 Operational Definition of Terms

- a) **Metals:-** Chemically, metals are defined as “elements, which conduct electricity, have a metallic luster, are malleable and ductile, formcations, and have basicoxides”. Terms usually used in relation to metals in biological and environmental studies are metal, metalloid, semimetal, light metal, heavy metal, essential metal, beneficial metal, toxic metal, abundant metal, available metal, trace metal, and micronutrient (Duffus, 2002).
- b) **Heavy Metals:-** According to Csuros and Csuros (2002),a heavy metal is defined as“ametalwithadensitygreater than 5g/cm³ (i.e., specific gravity greater than 5).” According to Duffus (2002), “the term “heavy metals” is

often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity.”

- c) **Toxicity:**-It refers to the property of a chemical to affect survival, growth, and reproduction of an organism. Certain heavy metals have been reported to be carcinogenic, mutagenic, and/or teratogenic to different species depending on dose and duration of exposure (Ali *et al.*, 2019).
- d) **Ecology:**- Is a branch of biology which studies the interactions among organisms and their environment. Objects of study mostly include biotic and abiotic components of the environment.
- e) **Public Health:**- Public health is a science and art of preventing disease, prolonging life and promoting human health through organized efforts and informed choices of society, organizations, public and private, communities and individuals. Analyzing the health of a population and the threats it faces is the basis for public health.
- f) **Water:**- It is said that water is the “life-blood of the biosphere.” Since water is a universal solvent, it dissolves different organic and inorganic chemicals and environmental pollutants. Aquatic ecosystems, both fresh water and marine, are vulnerable to pollution. Contamination of water resources by heavy metals is a critical environmental issue which adversely affects plants, animals, and human health. Heavy metals are extremely toxic to aquatic organisms even at very low concentrations (Rezania *et al.*, 2016).
- g) **Soil:**- Soil is a mixture of organic matter, minerals, gases, liquids and organisms that together support life. Earth’s body of soil, called the pedosphere, has four important functions: as a medium for plant growth, as a

means of water storage, supply and purification, as a modifier of Earth's atmosphere and as a habitat for organisms.

- h) **Vegetation:-** Vegetation is an assemblage of plant species and the ground cover they provide. It is a general term, without specific reference to particular taxa, life forms, structure, spatial extent, or any other specific botanical or geographic characteristics. It is broader than the term flora which refers to species composition; the closest synonym is plant community.
- i) **Spinach:** Spinach (*Spinacia oleracea*) is a leafy green flowering plant belonging to the order Caryophyllales, family Amaranthaceae. Its leaves are a common edible vegetable consumed either fresh, or after storage using preservation techniques such as freezing or dehydration. It may be eaten cooked or raw.
- j) **Pumpkin Leaf:-** It is locally known as "Ugu". *Telfairia occidentalis* is a tropical vine grown in West Africa as a leaf vegetable and for its edible seeds. It is a member of the family Cucurbitaceae and is mostly indigenous to Southern Nigeria, although it can equally be cultivated in the Northern parts of the country; and it is primarily used in soups and herbal medicines.
- k) **Waterleaf:-** *Talinum fruticosum* is a herbaceous perennial plant that is native to many parts of the world including West Africa. One of its common names is Ceylon spinach. It is mostly grown in tropical regions as a leaf vegetable because it is rich in vitamins and minerals. However, due to its high oxalic acid content, its consumption is limited.
- l) **Jute Leaves:-** Jute leaves are locally called Ewedu and are a part of the jute plant. The leaves have slightly toothed edges, and when harvested young,

jute leaves are generally flavourful and tender, while older leaves are fibrous and woody.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy Metals

Regarding their roles in biological systems, heavy metals are classified as essential and non-essential. Essential heavy metals are important for living organisms and may be required in the body in quite low concentrations. Non-essential heavy metals have no known biological role in living organisms. Examples of essential heavy metals are Mn, Fe, Cu, and Zn, while the heavy metals Cd, Pb, and Hg are toxic and are regarded as biologically non-essential (Rahim *et al.*, 2016). The heavy metals Mn, Fe, Co, Ni, Cu, Zn, and Mo are micronutrients or trace elements for plants. They are essential for growth and stress resistance as well as for biosynthesis and function of different biomolecules such as carbohydrates, chlorophyll, nucleic acids, growth chemicals, and secondary metabolites (Appenroth, 2010).

Either deficiency or excess of an essential heavy metal leads to diseases or abnormal conditions. However, the lists of essential heavy metals may be different for different groups of organisms such as plants, animals, and microorganisms. It means a heavy metal may be essential for a given group of organisms but non-essential for another one. The interactions of heavy metals with different organism groups are much complex (Ali *et al.*, 2019). Heavy metals are among the most investigated environmental pollutants. Almost any heavy metal and metalloid may be potentially toxic to biota depending upon the dose and duration of exposure. Many elements are classified into the category of heavy metals, but some are relevant in the environmental context. List of the environmentally relevant most toxic heavy metals and metalloids contains Cr, Ni, Cu, Zn, Cd, Pb, Hg, and As (Barakat, 2011).

Heavy metal pollutants most common in the environment are Cr, Mn, Ni, Cu, Zn, Cd, and Pb (Khan *et al.*, 2011). In 2009, China has suggested four metals, i.e., Cr, Cd, Pb, Hg, and the metalloid As, as the highest priority pollutants for control in the

12th5-year plan for comprehensive prevention and control of heavy metal pollution” reported in the recent reports of Fu and co-workers (2017). Some other heavy metals are also hazardous to living organisms depending upon dose and duration of exposure. For example, Mansouri *et al.* (2012) have found Ag as more toxic than Hg to a freshwater fish.

2.1.1 Sources of Heavy Metals in the Environment

Major sources of heavy metals in the environment can be both natural, geogenic, lithogenic and anthropogenic. The natural or geological sources of heavy metals in the environment include weathering of metal-bearing rocks and volcanic eruptions. The global trends of industrialization and urbanization on Earth have led to an increase in the anthropogenic share of heavy metals in the environment (Nagajyotiet *al.*, 2009). The anthropogenic sources of heavy metals in the environment include mining and industrial and agricultural activities. They are released during mining and extraction of different elements from their respective ores (Ali *et al.*, 2019).

Heavy metals released to the atmosphere during mining, smelting, and other industrial processes return to the land through dry and wet deposition. Discharge of wastewaters such as industrial effluents and domestic sewage add heavy metals to the environment. Application of chemical fertilizers and combustion of fossil fuels also contribute to the anthropogenic input of heavy metals in the environment. Regarding contents of heavy metals in commercial chemical fertilizers, phosphate fertilizers are particularly important (Tasuna *et al.*, 2015; Yang *et al.*, 2018).

In general, phosphate fertilizers are produced from phosphate rock (PR) by acidulation. In the acidulation of single superphosphate (SSP), sulfuric acid is used,

while in acidulation of triple superphosphate (TSP), phosphoric acid is used (Dissanayake and Chandrajith, 2009). The final product contains all of the heavy metals present as constituents in the phosphate rock. Commercial inorganic fertilizers, particularly phosphate fertilizers, can potentially contribute to the global transport of heavy metals (Odousoro *et al.*, 2010). Heavy metals added to agricultural soils through inorganic fertilizers may leach into groundwater and contaminate it. Phosphate fertilizers are particularly rich in toxic heavy metals. The two main pathways for transfer of toxic heavy metals from phosphate fertilizers to the human body are shown below (Nagajyotiet *al.*, 2010):

- i. Phosphate rock → fertilizer → soil → plant → food → human body
- ii. Phosphate rock → fertilizer → water → human body

Combustion of fossil fuels in industries, homes, and transportation is an anthropogenic source of heavy metals. Vehicle traffic is among the major anthropogenic sources of heavy metals such as Cr, Zn, Cd, and Pb. Higher concentrations of environmentally important heavy metals have been reported in soils and plants along roads in urban and metropolitan areas (Tasuna *et al.*, 2015). Regarding anthropogenic sources of heavy metals, emissions from coal combustion and other combustion processes are very important. During coal combustion, Cd, Pb, and As are partially volatile, while Hg is fully volatile (Khan *et al.*, 2004).

Interestingly, Lafia Local Government is being faced with many adverse environmental problems that affect the soil and gully erosion. This has slowed down the growth and development of the area in the last two decades, particularly economically. But, with intervention from both the state and local government

through construction of drainages in worst affected areas, the problem is ameliorating. In China for instance, combustion of coal is one of the major sources of atmospheric emissions of hazardous trace elements. The anthropogenic sources of Cr include electroplating industries, leather tanneries, textile industries, and steel industries (Tian *et al.*, 2013).

Globally, about 50,000t/year of Cr may be emitted from coal combustion, wood burning, and refuse incineration. Fertilizers also usually contain significant contents of Cr. Globally, about 60,000t/year of Ni may be generated from coal combustion; its greater portion remains in the ash (Krüger *et al.*, 2017). The natural sources of Cd in the environment are volcanic action and weathering of rocks, whereas an anthropogenic source is nonferrous metal mining, especially processing of Pb-Zn ores. Globally, about 7,000t/year of Cd may be emitted from coal combustion, and sewage sludge incineration is also a source of Cd. Anthropogenic increases in Cd concentrations are also caused by excessive application of chemical fertilizers. P-containing fertilizers contain Cd as a contaminant at concentrations ranging from trace quantities to 300ppm on dry weight basis and hence may be a main source of input of this metal to agricultural systems (Wang *et al.*, 2015).

Lead (Pb) is released to the environment from different sources including acid batteries, old plumbing systems, and lead shots used for hunting of game birds. Combustion of lead edgasolin eisalsoasource of Pb in the environment. Although use of the tetraethyl lead as an antiknock agent in gasoline has been banned, it is still used in some developing regions of the world (Ali *et al.*, 2019).

2.1.2 Heavy Metals as Hazardous Materials

Heavy metals are considered as hazardous chemicals in the environment. Nonessential heavy metals are toxic to plants, animals, and humans at very low concentrations. Even the essential heavy metals also cause adverse health effects at high concentrations (Mahboob *et al.*, 2014). Procedures developed for hazard identification of chemical contaminants in the aquatic environments consider three characteristic features: persistence, bioaccumulation, and toxicity. Usually, toxic substances which are both persistent and bioaccumulative are more hazardous (DeForest *et al.*, 2007).

Toxicity refers to the property of a chemical to affect survival, growth, and reproduction of an organism. Certain heavy metals have been reported to be carcinogenic, mutagenic, and/or teratogenic to different species depending on dose and duration of exposure. Heavy metals affect both wildlife and human health. Some species are more sensitive to heavy metals than others. The mechanisms by which heavy metals affect different organs, tissues, and systems in different organisms are very complex, and so far some of them are not fully explored (Mahboob *et al.*, 2014).

Exposure of the bivalve *Anodonta anatina* to Cd has been found to affect carbonic anhydrase (CA) in its tissues, an enzyme playing a role in osmoregulation and Ca metabolism. Cd has been considered as one of the factors likely responsible for the decline in populations of freshwater mussels due to its high toxicity, bioaccumulation potential, and transfer through food chains (Ngo *et al.*, 2011).

2.1.3 Heavy Metals Toxicity

Various usage of heavy metals in industry, agriculture, medicine and technology have led to their widespread distribution in nature raising concerns about their effects on human health and environment. The severity of toxicity arising from heavy metals, depends on various factors such as: dose, contact pattern, chemical species as well as age, sex, genetics and nutritional status of the person who is being contacted. Arsenic, chromium, cadmium, lead and mercury are important metals in relation to public health due to their high degree of toxicity. These metals are considered as systematic poisoning agents that can lead to organ failure even in exposure with lower dose. Hence, in recent years, concerns about public health and environmental pollution with these heavy metals are increased.

Human exposure to heavy metals has been increased in recent decades due to their widespread usage in industry. Also, environmental contamination in mining, casting and other related industrial areas are very significant (Mehrandish *et al.*, 2019). Metallic ions may interact with cellular components such as DNA and nuclear proteins leading to apoptosis and carcinogenesis arising from DNA damage and structural changes. Laboratory research has shown that reactive oxygen species and oxidative stress play a key role in the toxicity and carcinogenicity of heavy metals such as arsenic, cadmium, chromium, lead and mercury. These metals have a significant effect on general health, because of their systematic toxicity which can damage multi system organs, even at low doses (Beyersmann and Hartwig, 2008).

Various heavy metals and their physiological effects in body are shown in Table 1. Arsenic, cadmium, chromium, lead and mercury significantly contribute to environmental pollution. These elements enter human body through ingestion, inhalation and dermal contact to cause several health problems such as,

cardiovascular diseases, neurological and neurobehavioral abnormalities, diabetes, blood abnormalities and various types of cancer. The effects of these metals on human health depend on the type of metal and chemical type. Also these effects are time-dose dependent (Flora *et al.*, 2009). Several studies have shown that exposure to heavy metals causes long-term problems on human health. Some of these metals cause both acute and chronic toxicities. Recent studies have reported that these toxic elements may interact with some physiologically important metals such as iron calcium and zinc, to impair their normal metabolic function (Mehrandish *et al.*, 2019).

2.1.3.1 Arsenic Exposure

Arsenic is an element found in almost all environments in low concentrations. A large proportion of arsenic-containing compounds are manufactured industrially to be used in agriculture as pesticides, herbicides and fungicides. Also, these are used in veterinary to root out pumpkin worms in sheep and cattle herds. Arsenic compounds have long been used in medical sciences to treat diseases such as: syphilis, amoebic diarrhoea and trypanosome (Centeno *et al.*, 2006). Millions of people around the world appear to be constantly in contact with arsenic, especially in Bangladesh, India, Mexico and Taiwan, where ground water is contaminated with significant amount of arsenic. Arsenic pollution is a serious concern of public health. Several studies have found strong correlations between arsenic exposure and some pathological conditions including: cardiovascular diseases, peripheral vascular diseases, diabetes, hearing problems, blood abnormalities (anaemia, leukopenia, and eosinophilia) and cancer (Tchounwou *et al.*, 2004).

2.1.3.2 Cadmium Exposure

As a toxic trace element cadmium is highly capable of causing environmental and occupational hazard. Cadmium is widely used in battery industries and industrial workers dealing with this heavy metal are at high risk of cadmium poisoning through ingestion and inhalation which may damage digestive tract, lungs, liver and urethra and if severe, it can lead to coma and even death. Chronic exposure to cadmium suppresses norepinephrine, serotonin and acetylcholine levels and its inhalation triggers development of the pulmonary adenocarcinoma. Also, direct contact with cadmium can proliferate prostatic lesions including adenocarcinoma. There is evidence indicating that cadmium can damage DNA without free radical dependence. However, cadmium is less mutagenic than other metals (Satarug *et al.*, 2013).

2.1.3.3 Chromium Exposure

Chromium is known as a carcinogen and due to its widespread use in various industries, chromium can contaminate many of environmental systems. It is also found in industrial wastes. Occupational exposure is a major concern because of the high risk of chromium- induced diseases in industrial environments where the people are in contact with chromium type VI (Shelnutt *et al.*, 2007). Known as toxic agents, chromium VI containing compounds can damage various organs resulting in different diseases such as: kidney damage, allergies, asthma and respiratory tract cancer in human. The most common health problems caused by chromium I in animals include stimulation of stomach ulcer, sperm damage and disorders of male

reproductive system. The breakdown of DNA in peripheral lymphocytes and elevated lipid peroxidation products in the urine of chromium exposed patients, suggests that chromium VI could stimulate human poisoning (Goulart *et al.*, 2005).

2.1.3.4 Lead Exposure

Lead has a severe toxic effect on multi organ systems including: liver, kidney, central nervous system and reproductive system. However, lead poisoning manifests with different complications in children and adults. There is a direct relationship between blood lead levels and decreased intelligence quotient, neurodegenerative deficits and hearing loss in children. Acute lead poisoning in adult persons triggers brain damage, kidney damage and digestive system diseases, while, chronic exposure to lead can affect blood cells, central nervous system, kidney and vitamin D metabolism. Also, lead enters bone structure, through combination with bone minerals. Evidences have shown that lead poisoning can stimulate cellular degradation through production of reactive oxygen species (Flora *et al.*, 2007).

2.1.3.5 Mercury Exposure

Mercury is found in three forms in nature: elemental, organic and inorganic, all of which exhibit different behaviour in terms of toxicity. Widely distributed in nature, mercury is a toxic element. This metal affects human health by causing severe changes in tissues (Mehrandish *et al.*, 2019). Due to its wide distribution in nature, exposure to some chemical forms of mercury is inevitable. Due to very low excretion rate, a large percentage of absorbed mercury accumulates in kidneys, nerve tissue and the liver. All chemical forms of mercury are poisonous and cause

gastrointestinal poisoning, neurological and kidney toxicities. Oxidative damages caused by mercury poisoning arise from accumulation of reactive oxygen species that are eliminated by normal antioxidants in normal state. Mercury stimulates the formation of reactive oxygen species, causing DNA damage and carcinogenesis (Flora *et al.*, 2010).

2.1.3.6 Heavy Metal Toxicity Treatment

The first step in treatment of heavy metals poisoning, is to eliminate the source of exposure and to keep the patient away from the exposure source. Trevor and colleagues in 2010 deduced that the first-line therapy is symptomatic and supportive treatment and in the process, strict monitoring of the various organs of the body including kidney, liver, respiratory and cardiovascular systems should be carried out. Generally, administration of chelating agents is the most common therapy (Trevor *et al.*, 2010).

Recently, medicinal herbs have attracted the attention of researchers as the potential treatments for the heavy metals poisoning. Some herbs contain chelating agents which reduce the bioavailability and gastrointestinal absorption of heavy metals. Moreover, herbal treatments can decrease the bioavailability of toxic substances by increasing the gastrointestinal movements resulting in faster excretion of toxicants through the faeces as reported by Mehrandish *et al.* (2019).

This can be considered as an auxiliary method to reduce the effects of poisoning with heavy metals if ingestion is the route of exposure. According to previous findings, such as those of Nwokocha *et al.* (2012) and Hewlings and Kalman

(2017),“regular consumption of herbal products, may significantly reduce the absorption of heavy metals”.

2.2 Human Exposure to Heavy Metals

Humans are exposed to toxic heavy metals in the environment through different routes including ingestion, inhalation, and dermal absorption. People are more exposed to toxic metals in developing countries (Egani *et al.*, 2016). Generally, people have no awareness and knowledge about exposure to heavy metals and its consequences for human health, especially in the developing countries. People may be exposed to heavy metals in the work place and in the environment (Afrin *et al.*, 2015).

Human exposure to toxic chemicals in the work place is called occupational exposure while exposure to such chemicals in the general environment is called non-occupational or environmental exposure. Workers are exposed to heavy metals in mining and industrial operations where they may inhale dust and particulate matter- containing metal particles. People extracting gold through the amalgamation process are exposed to Hg vapours. It has been reported that welders with occupational prolonged exposure to welding fumes had significantly higher levels of the heavy metals Cr, Ni, Cd, and Pb in blood than the control and showed increased oxidative stress (Mahmood *et al.*, 2015).

Cigarette smoking is also a principal source of human exposure to Cd and other toxic heavy metals present in the tobacco leaves. Ingestion of heavy metals through food and drinking water is a major exposure source for the general human population. Industrialization, urbanization, and the rapid economic development

around the globe have led to intensification in industrial and agricultural activities. Such activities may cause contamination of water, air, and soils with toxic heavy metals (Järup, 2003).

Interestingly, growing human foods in heavy metal-contaminated media lead to bioaccumulation of these elements in the human food chains from where these elements ultimately reach the human body (Järup, 2003; Tasuna *et al.*, 2015; Vongdala *et al.*, 2019).

Table 2.1: Physiological Importance of Heavy Metals

Metals	Biological Significance
Iron	Oxygen transportation; Plays a role in metabolism as a component of some proteins and enzymes.
Zinc	Participates in drug metabolism, in mobilizing vitamin A from the liver, and In a defense system in microorganisms against free radical damages.
Copper	Plays an important role in our metabolism, is essential for maintaining the strength of the skin, blood vessels, it epithelial and connective tissue throughout the body.
Chromium	Important in the metabolism of fats and carbohydrates. It stimulates fatty acid and cholesterol synthesis. Also, it is involved in insulin action and glucose metabolism.
Cobalt	An essential part of vitamin B12 and involved in hematopoiesis
Molybdenum	Act as an electron carrier in those enzymes that catalyzing the reduction of nitrogen and nitrate. Is needed for at least three enzymes. Sulfite oxidase catalyses the oxidation of sulfite to sulfate, necessary for metabolism of sulfur amino acids.
Selenium	A functional mineral in immune system.
Manganese	Plays a Role in the Metabolism of macronutrients. It helps with protein and amino acid digestion and utilization, as well as the metabolism of cholesterol and carbohydrates
Magnesium	It is important in energy production and maintaining electrolyte balance. Is essential for normal neuromuscular functions as well as calcium and potassium transport
Therapeutic Effects	
Arsenic, Platinum, Ruthenium	Anti-cancer
Bismuth	Stomach ulcer

Gold Anti-arthritis

Iron Anti-malaria

Copper, Zinc, Gold, Silver Anti-inflammatory

Harmful Effects

Mercury Reduced sensory abilities, fatigue, anorexia, irritability and excitability, cardiovascular disease, hypertension with renal dysfunction.

Cadmium Anaemia, hair loss, hypertension, kidney problems

Lead In children: delayed mental development, hyperactivity.

In adults: fatigue, anaemia, metallic taste, loss of appetite, weight loss and headaches, insomnia

Arsenic Fatigue, headaches, dermatitis, increased salivation, muscular weakness, loss of hair and nails

Ref. Mehrandish *et al.* (2019).

2.3 Pollution of Water by Heavy Metals

2.3.1 Worldwide Overview

Pollution is defined as the introduction of elements, compounds or energy into the environment at concentrations that impair its biological functioning or that present an unacceptable risk to humans or other targets that use or are linked to the environment, while heavy metals are common pollutants which might be found in drinking water throughout the seven continents arising scientific and public concern on human health. The continents identified by convention rather than any strict criteria are (from largest in size to smallest): Asia, Africa, North America, South America, Antarctica, Europe and Oceania (Fernández-Luqueño *et al.*, 2013).

2.3.2 Pollution within the Asian Continent

Asia is the largest continent on Earth in which China, Bangladesh, Vietnam, Taiwan, Thailand, Nepal and India are located, seven countries where environmental concerns are arising because large amounts of heavy metals have been found in drinking water. In these countries, arsenic is found at high concentration in groundwater, drinking water and surface soil (Chen, 2006). Roychowdhury *etal.* (2003) reported that in India, the arsenic concentration ($107 \mu\text{gL}^{-1}$) in drinking water was approximately 11 times higher than the World Health Organization (WHO) guideline value (WHO, 2008), while concentrations of copper, nickel, manganese, zinc and selenium were lower than the WHO guideline values.

Furthermore, Chatterjee *etal.* (1995), found as, in ground water above the maximum permissible limit in six districts of West Bengal, India, covering an area of 34000 km^2 with a population of 30 millions. Ten years later, on the same area, Von Ehrenstein *etal.* (2005) revealed that consumption of arsenic-contaminated water was associated with respiratory symptoms and reduce lung function in men, especially among those people with arsenic-related skin lesions, while Borah *et al.* (2010) stated that the drinking water sources in Assam, India, are heavily polluted with lead. Additionally, Borah *etal.* (2010) reported that iron content in the drinking water sources in that area exceeds the WHO guideline value of $0.3 \mu\text{gL}^{-1}$. Chaudhary and Kumar (2009) revealed that in the villages around Kali River (India), 22 samples exceeded the limit of iron ($0.3 \mu\text{gL}^{-1}$) and the possible sources of the high iron content in drinking water are various iron industries located close to Kali river.

Therefore, it has been reported that uranium was found to be more than the safe limit in drinking water samples from India (Kumar *et al.*, 2006) and Finland (Prat *et al.*, 2009), while Frisbie *et al.* (2009) demonstrated that some tube wells from Bangladesh had concentrations exceeding WHO health-based drinking water guidelines were U, Mn, As, Pb, Ni and Cr. Additionally, Lodhi *et al.* (2003) reported that heavy metal concentrations in drinking water from Skardu, Pakistan, followed the order $Zn > Fe > Ni > Pb > Co > Cu > Cr$ but no survey regarding the portability of water has been conducted in the past.

Furthermore, Nickson *et al.* (2005) revealed that drinking water sampled in Muzaffargarh, Pakistan, reached up to $906 \mu\text{g L}^{-1}$ As and that in 58% of samples $> 10 \mu\text{g L}^{-1}$ As were found. Moreover, Maharjan *et al.* (2005) argued that the tube wells are the only source for drinking water in Terai, Nepal, where As ranged from 3 to $1072 \mu\text{g L}^{-1}$ with a mean of $403 \mu\text{g L}^{-1}$, therefore, arsenicosis victims counts up 6.9% of Nepalese population resides. Likewise, Buschmann *et al.* (2007) reported seasonal fluctuations in the arsenic concentration (from 1 to $1340 \mu\text{g L}^{-1}$) in drinking water from wells in Cambodia. In addition, they stated that regions exhibiting low and elevated arsenic levels are co-incident with the present low relief topography featuring gently increasing elevation to the west and east of a shallow valley understood as a relict of pre-Holocene topography.

In Vietnam, Buschmann *et al.* (2008) stated that groundwater contamination is of geogenic origin and caused by natural conditions in the aquifers. In this area, chronic arsenic poisoning is the most serious health risk for the similar to 2 million people drinking this groundwater without treatment, followed by malfunction in children development through excessive manganese uptake. Additionally, high

concentrations of Ba, Cd, Ni, Se, Pb and U were presents too. In Sri Lanka, cadmium is one of the most troublesome toxic heavy metals which accumulate in the water reservoirs and agricultural soil as a result of intensive use of Cd contaminated phosphate fertilizers that causes chronic renal failure (Bandera *etal.*, 2010). It is known that Cd is the heavy metal of most environmental concern in terms of adverse effects from long-term application of phosphate fertilizers.

Limbong *etal.* (2004) found concentrations of mercury in drinking water from Indonesia very close to values established by WHO. Additionally, Cortes-Maramba*etal.* (2006) revealed that notwithstanding, in Philippines, levels of mercury in drinking water and sediments were within allowable, limits the frequency of gastrointestinal complaints, was significantly associated with elevated hair methylmercury levels. It is known that more than 60,000,000 Bangladeshis are drinking water with unsafe concentrations of one or more elements such as As, Mn, U, Pb, Ni and Cr (Frisbie *etal.*, 2009) notwithstanding the WHO efforts to improve their water quality.

Xu *etal.* (2006) reported that the mean concentrations of Cu, Zn and As in drinking water from Shangai, China were 10.8 μgL^{-1} , 0.29 mgL^{-1} and 0.91 μgL^{-1} , respectively; which were lower than United States Environmental Protection Agency (USEPA) and WHO guideline values. Chiba and Fukuda (2005) found that uranium concentrations were high in the water samples of the Central Asian countries including east side of the Aral Sea, Kazakhstan, while a high prevalence of renal dysfunction was also reported by them.

2.3.3 Pollution within the African Continent

Africa is the second-largest of the world and second most-populous continent, after Asia. Africa suffers from many environmental problems including deforestation, degradation, desertification, air and water pollution, the loss of soil fertility, a dramatic decline and loss of biodiversity. Asante *et al.* (2007) reported contamination by As, Mn, Hg and Pb in drinking water from Tarkwa, Ghana. Several water samples showed As and Mn concentrations above the WHO guideline values for drinking water, suggesting that human health risk is a great concern for those metals. Similar results were found by Buamah *etal.* (2008) in groundwater within the gold-belt zone of Ghana. They collected and analyzed 290 well water samples and stated that 5 to 12% of sampled wells had arsenic levels exceeding the WHO guideline value. Eighty per cent of wells exceeded $0.3 \text{ mgL}^{-1}\text{Fe}$, the drinking water guideline value for iron and 42% exceeded $0.1 \text{ mgL}^{-1} \text{Mn}$, the WHO health-based guideline value for manganese.

Dzoma *etal.* (2010) stated that water samples from Koekemoerspruit, Africa have As and Cd levels of 12 and $10\mu\text{gL}^{-1}$, respectively, those levels are several magnitudes higher than the WHO maximum permissible levels for drinking water of 10 and $3\mu\text{gL}^{-1}$, respectively.

2.3.4 Pollution within the North American Continent

In this continent, water pollution is becoming a bigger issue. Pollution from farms, factories and even the water conducts may contaminate drinking water. High concentrations of Cu (88 to $147\mu\text{gL}^{-1}$) and Ni (16 - $35\mu\text{gL}^{-1}$) were found in bottled drinking waters sold in Canada (Dabeka *etal.*, 2002) while McGuigan *et al.* (2010)

reported that in some provinces and territories from Canada that is, Alberta, British Columbia, Manitoba, New Brunswick, Newfoundland and Labrador, Nova Scotia, Quebec, and Saskatchewan have been found concentrations of As above $10\mu\text{gL}^{-1}$, the current guideline level of the Federal Provincial-Territorial Committee on Drinking Water. It is known that inorganic arsenic is naturally occurring in groundwater throughout the United States (Zierold *et al.*, 2004), such as several national assessments have found that high arsenic concentrations ($> 10\mu\text{gL}^{-1}$) are widespread in drinking water aquifers in the western United States, the Great Lakes region and New England (Ryker, 2003).

Chemical data from more than 400 groundwater sites in the Middle Rio Grande Basin of central New Mexico indicate that arsenic concentrations exceed $10\mu\text{gL}^{-1}$ across broad areas of the Santa Fe Group aquifer system, which is currently the most exclusive source of drinking water supply for residents of the basin (Bexfield and Plummer, 2003). Peters *et al.* (2006) pointed out the importance of quantifying arsenic exposure from private water supplies and reported that domestic bedrock wells supply water to 120,000 households, with a median arsenic concentration of $1.9\mu\text{gL}^{-1}$, domestic surficial wells provide water to approximately 40,000 households with a median arsenic concentration of $0.15\mu\text{gL}^{-1}$, and municipal water systems provide water to 265,000 households with a median arsenic concentration of $0.41\mu\text{gL}^{-1}$.

Nevertheless, Erickson and Barnes (2005) stated that in the upper Midwest, USA, elevated arsenic concentrations in public drinking water systems are associated with the lateral extent of northwest provenance late Wisconsin-aged drift, where twelve percent of public water systems located within the footprint of this drift (212 of

1764) exceed $10\mu\text{gL}^{-1}$ As, the USEPA drinking water guideline value. This suggests that high-arsenic sediment is not necessary to cause arsenic-impacted ground water because leaches, bedrocks, depth and human activities are also important factors that increase the heavy metals pollution in drinking water. Lytle *et al.* (2004) stated that it is well known that the use of iron solid surfaces to adsorb arsenic has become the basis for several drinking water treatment approaches that remove arsenic.

It is reasonable to assume that iron- based solids such as corrosion deposits present in drinking water distribution systems have similar adsorptive properties and could therefore concentrate arsenic and potentially re-release it into the distribution system. They found in iron-based solids collected from drinking water distribution systems located in Ohio, Michigan and Indiana arsenic contents ranged from 10 to $13,650\mu\text{g g}^{-1}$ solids. The concentrations of trace elements in water from Tuskegee Lake (South Eastern of United States) were investigated by Ikem *et al.* (2003), they found that the water quality characteristics were mostly below the recommended drinking water standards by the USEPA and the European Union (EU) except for aluminium, iron, manganese and thallium. In addition, the average values of Cr, As, Mn, Zn and Cl⁻ in the water samples analyzed were higher than the respective reference values for fresh water.

Similarly, it has been reported that in Mexico, natural groundwater As contamination ranked 0.5 to 3.7mgL^{-1} (Hossain, 2006). However, Wyatt *et al.* (1998) reported that drinking water samples of wells or storage tanks from Northern Mexico, that is, Sonora State, had $117\mu\text{gL}^{-1}$ As, 50 to $120\mu\text{gL}^{-1}$ Pb, and 1 to $25\mu\text{gL}^{-1}$ Hg, which appears that As, Hg and Pb contamination in drinking water for this area is a major concern. Camacho *et al.* (2011) stated that in the states of Coahuila

and Chihuahua, Mexico, high As concentrations were found mainly in groundwater, their source being mostly from natural origin related to volcanic processes with significant anthropogenic contributions near mining and smelting of ores containing arsenic. Some details of heavy metal-polluted drinking water from Mexico can be found in Armienta and Segovia (2008), Camacho *et al.* (2011) and McClintock *et al.* (2012).

2.3.5 Pollution within the South American Continent

Marshall *et al.* (2007) found that drinking water in region II of Chile is supplied mainly by rivers that contain inorganic arsenic at very high concentrations. Before 1958, the arsenic concentration in the water supply in the main city of region II, Antofagasta, was approximately $90\mu\text{gL}^{-1}$, nearly twice the drinking water standard in much of the world ($50\mu\text{gL}^{-1}$) until the recent lowering of the level in some countries to $10\mu\text{gL}^{-1}$ in the mayor cases. Garcia-Sanchez *et al.* (2008) reported that in the Coyuni river basin (Venezuela), artisanal gold mining has caused significant mercury pollution due to the extensive use of Hg in the Au amalgamation processes. They recorded high Hg concentrations up to $4.6\mu\text{gL}^{-1}$ in surface water samples which exceeds the USEPA recommended value of $2\mu\text{gL}^{-1}$.

Madrakian and Ghazizadeh (2009) detected > 1.1 and $< 2.4\mu\text{gL}^{-1}$ Sn(IV) in water samples from Brazil. De Figueiredo *et al.* (2007) revealed that integrated studies on environmental and anthropogenic sources of As contamination have been carried out only in three areas from Brazil:

- 1) The Southeastern region known as the Iron Quadrangle, where As was released into the drainage systems, soils and atmosphere as a result of gold mining;
- 2) The Ribeira Valley, where As occurs in Pb-Zn mine wastes and naturally in As-rich rocks and soils;
- 3) The Amazon region, including the Santana area, where As is associated with manganese ores mined over the last 50 years.

However, they argued that toxicological studies revealed that the populations were not exposed to elevated levels of As, with the As concentrations in surface water in these areas rarely exceeding $10 \mu\text{g L}^{-1}$. A possible reason is the deep weathering of bedrocks along with formation of Fe/Al-enriched soils and sediments function as a chemical barrier that prevents the release of As into water.

In addition, the tropical climate results in high rates of precipitation in the northern and southeastern regions and, hence, the As contents in drinking water is diluted. Alonso *et al.* (2006) found concentrations of aluminium, arsenic, manganese and iron above the guideline values of WHO in drinking water from Bolivia. Recently, the arsenic exposure in Latin America has been reviewed by McClintock *et al.* (2012), they estimated that at least 4.5 million people in Latin America are chronically exposed to high level of As that is $>50\mu\text{gL}^{-1}$, and some as high as $2000\mu\text{gL}^{-1}$ As.

2.3.6 Pollution within the Antarctic Continent

The Antarctica is a terrestrial continent covered in 98% by ice that averages at least 1.6km in thickness and it has reached a temperature -89°C . It is considered a desert, with annual precipitation of only 200mm along the coast and far less inland. Although, Antarctica does not have stream-river drainage systems, there are many sub-glacial and sub-aerial lakes, and the summer melting of snow banks or glacier ice may originate small seeps and ephemeral streams in coastal areas (Bargagli, 2008). Nevertheless, Antarctica is often considered as one of the last pristine regions, metals, organic compounds, invasive species and other contaminants enter the continent through air, water, bird, marine mammals and by anthropogenic activities (Hughes and Convey, 2012).

Significant interannual variations in physical characteristics of the surface waters, such as sea-ice coverage and melt water percentage, can affect both the stability of the water column and the trace metal distribution and speciation. Heavy metals such as V, Cr, Mn, Cu, Zn, Co, Ag, Cd, Ba, Pb, Bi and U have been measured in a series of dated snow samples, covering the period from 1834 to 1990, collected at remote, low accumulation sites in Coats Land, Antarctica, but concentrations are found to be extremely low, down to $3 \times 10^{-15}\text{gg}^{-1}$ for most metals, then confirming the high purity of Antarctic snow (Rivaro *et al.* 2011).

Natural processes such as volcanic activity, hydrothermal processes and sediment transport are more important than anthropogenic inputs in accounting for the metal concentrations measured in sediments at different places. Findings show that human activities in the study areas may contribute to negligible levels of trace metals associated with anthropogenic inputs (for example, Cr and Zn) in sediments. Eolian

deposition from strong winds contributes in an important way to the trace metallic elements content onto Antarctic dry valley glacier snow and glacier melt ecosystems, including supra and proglacial streams. It is known that lithogenic material is the dominant source of As, Cd, Cu, Mo, Pb, Sn and Sb to snow (for example, Taylor Valey)(Guerra *etal.*, 2011).

Comparisons of distributions of As, Mo, Cu and Pb between snow and supra and proglacial melt streams suggest that eolian deposition is a major source of these elements to Antarctic dry valley aquatic ecosystems (Fortner *etal.*, 2011). Mercury is a globally dispersed toxic metal that affects even remote polar areas, for example, during seasonal atmospheric mercury depletion events in polar areas, mercury is removed from the atmosphere and subsequently deposited in the surface snows, mainly coldest climatic stages (Jitaru *etal.*, 2009).

2.3.7 Pollution within the European Continent

Kelepertsis *etal.* (2006) found elevated concentrations of As ($125 \mu\text{g L}^{-1}$) and Sb ($21 \mu\text{g L}^{-1}$) in the drinking water of Eastern Thessaly, Greece, where more than 5,000 people drink water containing As and Sb above the USEPA guidelines, while recently, Jovanovic *etal.* (2011) found that 63% of all water samples exceeded Serbian and European standards for arsenic in drinking water and Cavar *etal.* (2005) reported that in three villages from eastern Croatia, the mean arsenic concentrations in drinking water samples were 38, 172 and $619 \mu\text{g L}^{-1}$ which could present a serious health threat to around 3% of Croatian population.

Tamasi and Cini (2004) found in South Tuscany, Italy, that As concentrations were relatively high in drinking water sampled from the ends of the distribution lines

when compared to values at sources, showing that the quality of drinking water in town is somewhat worse than that at one of the main sources, probably due to leaching from metal pipes. Similar results were found by Etxabe *et al.* (2010) in Spain and Haider *et al.* (2002) in Austria, they concluded that lead concentration in drinking water increased as it is released from piping.

Tsoumbaris *et al.* (2009) revealed that in several samples of drinking water from north-eastern Greece, manganese and iron concentrations exceeded the acceptable limits for potable water set by the Hellenic Joint Ministerial Act Y2/2600/2001 'quality of the water intended for human consumption'. Additionally, Rajkovic *et al.* (2008) reported the presence of radioactive elements of uranium and strontium of anthropogenic origin in drinking water-samples of the water-supply network from Belgrade, Serbia. Nielsen (2009) reported that in Denmark, nickel was detected in 3,362 wells and in 221 wells; the local current drinking water limit at $20\mu\text{gL}^{-1}$ was exceeded.

However, it has to be remembered that the current WHO drinking water guideline is $70\mu\text{gL}^{-1}$ Ni. A total of 908 bottled water samples and 164 tap water samples were analyzed for heavy metals and their results showed that 4.63% (42 samples) of all bottled water samples exceed the limits for one or more of the following elements: arsenic (9 samples), manganese (eight samples), nickel (1 sample) and barium (1 sample). Moreover, ten of the samples exhibited uranium concentrations above $10\mu\text{gL}^{-1}$ and 127 samples yielded $> 2.0\mu\text{gL}^{-1}$ U (Birke *et al.*, 2010). They also analyzed the Te concentrations in bottled water which varies between < 0.005 and $0.21\mu\text{gL}^{-1}$, while in the tap water between < 0.005 and $0.025\mu\text{gL}^{-1}$. The maximum Te concentration measured in surface water in Germany was $0.073\mu\text{gL}^{-1}$.

Other authors have observed values between 0.00017 and 0.073 μgL^{-1} Te in surface water (Sugimura and Suzuki, 1981) and ranged values between 0.00051 and 0.0033 μgL^{-1} Te in rain water (Andreae, 1984). Although, in Germany, <0.6% of all households are estimated to receive drinking water exceeding the threshold level of 10 μgL^{-1} U, up to 75 μgL^{-1} U have been measured in Bavaria (Friedmann and Lindenthal, 2009). Prat *et al.* (2009) reported that elevated concentrations of uranium have been measured in water samples from private wells in residential communities in different countries throughout the world (Greece, Australia, U.S. and Germany). Moreover, they found exceptionally high natural concentrations in drinking water originating from drilled wells in Southern Finland (from 37 to 3,410 μgL^{-1} , that is, reach more than 100 times those given in the current WHO guideline of 30 μgL^{-1}), but no clear clinical symptoms have been observed among the exposed population.

2.3.8 Pollution within the Oceania Continent

In countries such as Australia and New Zealand, the presence of heavy metals in water systems is of local significance. In these countries, strict quality guidelines have been developed, particularly for protection of aquatic ecosystem. Presence of heavy metals in the Oceania continent is due to both natural and anthropogenic origin. It has been found the presence of various naturally-occurring radium isotopes in water samples from saline seepages from Australia (Hart *et al.*, 1999).

The distribution of Cu, Pb and Zn have been studied in aquatic systems draining Mount Isa Mine in arid northern Queensland, Australia, the delivery of heavy metals to riverbanks and dust entrainment in arid zones may concentrate heavy metal and ultimately ingested and absorbed by biota (Taylor and Hudson-Edwards, 2008).

Other important source of contaminations has been detected in Lake Burragorang, where high concentration of Cu, Pb and Zn (204, 332 and 2460 $\mu\text{g g}^{-1}$, respectively) were found in fluvial sediment, this issue was associated to sewage treatment plant.

Additionally, coal-based power stations contribute considerable to Cu, Ni, Co and Cr pollution (562, 157, 113 and 490 $\mu\text{g g}^{-1}$, respectively) in fluvial sediments (Birch *et al.*, 2001). In Australia, rainwater harvesting is typically used to supplement tap water in Auckland, New Zealand, a cross-sectional survey was realized to determine heavy metal concentration and microbiological content, it was found that 17.6% of the examined collection points exceeded one or more of the maximum guideline values for heavy metal of the New Zealand Drinking Water Standards (NZDWS), and 56.0% points exceeded the microbiological criteria of <1 FC/100 ml. 14.4% exceeded the NZDWS for lead and copper. It is known that in Australia, a principal source of drinking water is the rainwater, however, it has been found that there exist some health risks linked to heavy metals if untreated rainwater is consumed (Chang *et al.*, 2004).

There are no drinking water quality guidelines for bismuth, cerium, cobalt, gallium, gold, platinum, tellurium, tin and vanadium (USEPA, 2011; WHO, 2011; Fernández-Luqueño *et al.*, 2013)

Table 2.2: Current Drinking Water Quality Guidelines (μgL^{-1}) for Heavy Metals ()

Heavy Metal	WHO ^a	USEPA ^b	ECE ^c FTP-	CDW ^d	PCRWR ^e	ADWG ^f	NOM-127 ^g
Antimony	20	6	5	6	5	3	–
Arsenic	10	10	10	10	50	10	25
Cadmium	3	5	5	5	10	2	5
Chromium	50	100	50	50	50	50	50
Copper	2000	1300	2000	1000	2000	2000	2000
Iron	–	300	200	300	–	300	300
Lead	10	15	10	10	50	10	10
Manganese	100	50	50	50	500	500	150
Mercury	6	2	1	1	1	1	1
Nickel 70	–	20	–	20	20	–	–
Silver	–	100	–	–	–	100	–
Thallium	–	2	–	–	–	–	–
Uranium	30	30	–	20	–	17	–
Zinc	–	500	–	5000	5000	3000	5000

Keys: a= World Health Organization (WHO 2011); b= United States Environmental Protection Agency (USEPA, 2011); c= European Commission Environment (ECE, 1998); d= Federal-Provincial-Territorial Committee on Drinking Water (CDW), Health Canada (FTP-CDW, 2010); e= Pakistan Council of Research in Water (PCRWR, 2008); f= Australian Drinking Water Guidelines (DDWG, 2011); g= Norma Oficial Mexicana NOM-127-SSA1-1994 (DOF, 1994).

Citation: Fernández-Luqueño *et al.* (2013).

2.4 Public Health Risks of Heavy Metal–Contaminated Soil

Heavy metals in soils are of great concern to humans and the environment, due to their toxicity, bio-accumulative potentiality, biodegradability, and recalcitrant nature (Aluko *et al.*, 2018). Heavy metals and metalloids are released into soils from the parent material (lithogenic source) and different anthropogenic sources. Factors affecting the presence and distribution of heavy metals in soils include composition of parent rock, degree of weathering, and physical, chemical, and biological characteristics of soil and climatic conditions (Alloway, 2013). The bioavailability of heavy metals in soils is very important for their fate in the environment and for their uptake in plants. Different heavy metals have different bio availabilities in soils, and this bioavailability is dependent on metal speciation and on different physicochemical properties of soils (Ali *et al.*, 2019).

Major mechanisms of transfer of heavy metals from the mining sites take place via the air, ground water sources, and surface water body. Also, irrigation with contaminated groundwater and river water are responsible for soil contamination. Heavy metal and metalloid pollution of farmland and crops can substantially impact food safety as well as human health (Islam *et al.*, 2018). Industrial wastes and pesticides had also contributed to soil heavy metal contamination where untreated effluents from the industries are directly adding heavy metals and metalloids into nearby water and soil. On the same note, mining has an impact on soil heavy metal load (Flanagan *et al.*, 2012).

However, accumulation of these metals in soil, air, water, and edible parts of plants represents a direct pathway for their entry into human food chain. Although no health risk studies have ever been conducted in these mining areas, children and

adults of mining communities have often reported incidents of chest pain, tuberculosis, diarrhoea, cough, and itchy skin (Kamunda *et al.*, 2016).

Some metals are essential for life, playing an irreplaceable role as sources of vitamins and minerals for human organs to function. All living organisms require varying amounts of metals, but at higher concentrations they become toxic (Adesuyi *et al.*, 2015). What is more, some metals do not play any useful role in human physiology and might be toxic even at low rates of exposure. They might continuously get accumulated in vital organs such as the brain, the liver, bones, and kidneys, for years or decades, in turn causing serious health problems (Kabata-Pendias, and Pendias, 2011).

Lead (Pb) is the second hazard in the priority list of heavy metal pollutants, designated by United States Agency for Toxic Substances and Disease Registry (2007). Regarded as a human mutagen and probable carcinogen (Podsiki, 2008), it is well-known to induce renal tumours, and disturb normal function of kidneys, joints, reproductive, and nervous systems (Kamunda *et al.*, 2016). Acute ingestion of Cd is also known to be toxic, even in low amounts, being regarded as a probable carcinogen as well. Severe exposure to Cd may result in pulmonary effects such as alveolitis, bronchiolitis, and emphysema (Adedokun *et al.*, 2016). It can also result in bone fracture, kidney dysfunction, hypertension, and even cancer. What is more, some of its odd long-term effects include arthritis, diabetes, anaemia, cardiovascular disease, cirrhosis, reduced fertility, headaches, and strokes. Zn and Cu are essential for human life, yet excessive intake of these metals may have non-carcinogenic impacts on human health (Kamunda *et al.*, 2016).

In the same vein, higher concentrations of Zn have been associated with growth and reproduction impairment, whereas higher amounts of Cu are associated with liver damages (Adesuyi *et al.*, 2015; Kamunda *et al.*, 2016). While Chromium (III) is an essential element, chromium (VI) compounds are known to be mutagenic and carcinogenic. Inhaling high levels of chromium (VI) may cause asthma and shortness of breath. Also, long-term exposure to it might damage the liver and the kidneys (Podsiki, 2008). Ni, on the other hand, is known to cause cancer, both orally and intestinally. It is also responsible for health issues such as depression, heart attacks, haemorrhages, and kidney problems (Aluko *et al.*, 2018).

2.5 Effects of Heavy Metals Contamination on Plants and Vegetation

Environmental pollution and nature of the soil directly affect the heavy metal and metalloid content in vegetation and by extension foods grown on agricultural land. Chemical pesticides and fertilizers containing heavy metals and metalloids are both major sources of heavy metals and metalloids in foods. Some trace metals are essential in plant nutrition; however, excess heavy metals and metalloids can accumulate in various edible and non-edible parts of plants (Islam *et al.*, 2018). Some of these heavy metals i.e. As, Cd, Hg, Pb or Se are not essential for plants growth, since they do not perform any known physiological function in plants. Others i.e. Co, Cu, Fe, Mn, Mo, Ni and Zn are essential elements required for normal growth and metabolism of plants, but these elements can easily lead to poisoning when their concentration greater than optimal values (Singh and Khamdhad, 2011).

The use of compost to improve agricultural yield without caring with possible negative effects might be a problem since the waste composts are most applied to

improve soils used to grow vegetables. Considering the edible part of the plant in most vegetable species, the risk of transference of heavy metals from soil to humans should be a matter of concern. Uptake of heavy metals by plants and subsequent accumulation along the food chain is a potential threat to animal and human health (Singh and Khalamdhad, 2011). The absorption by plant roots is one of the main routes of entrance of heavy metals in the food chain. Absorption and accumulation of heavy metals in plant tissue depend upon many factors which include temperature, moisture, organic matter, pH and nutrient availability. The uptake and accumulation of Cd, Zn, Cr and Mn in *Beta vulgaris* (Spinach) were higher during the summer season, whereas Cu, Ni, and Pb accumulated more during the winter season (Singh *et al.*, 2010).

It may be expected that during the summer season the relatively high decomposition rate of organic matter is likely to release heavy metals in soil solution for possible uptake by plants. The higher uptake of heavy metals i.e. Cd, Zn, Cr and Mn during the summer season may be due to high transpiration rates as compared to the winter season due to high ambient temperature and low humidity. Heavy metal accumulation in plants depends upon plant species and the efficiency of different plants in absorbing metals is evaluated by either plant uptake or soil to plant transfer factors of the metals. Elevated Pb in soils may decrease soil productivity, and a very low Pb concentration may inhibit some vital plant processes, such as photosynthesis, mitosis and water absorption with toxic symptoms of dark green leaves, wilting of older leaves, stunted foliage and brown short roots (Singh and Khalamdhad, 2011). Heavy metals are potentially toxic and phytotoxicity for plants resulting in chlorosis, weak plant growth, yield depression, and may even be

accompanied by reduced nutrient uptake, disorders in plant metabolism and reduced ability to fixate molecular nitrogen in leguminous plants (Sobha *et al.*, 2007).

Basically, leafy vegetables are more liable to heavy metal and metalloid contamination, due to their rapid growth and direct transfer of metals and metalloids to the leafy parts (Mingorance *et al.*, 2007). Also, Chang and others (2014) deduced that irrigation with heavy metal contaminated ground water is another primary cause of food heavy metal–contamination in many parts of the world. It is plausible to note therefore that irrigation with contaminated river water may substantially affect the metal and metalloid concentrations of vegetables.

Ahmad *et al.* (2010) found red amaranth (*Amaranthus cruentus*) from agricultural land surrounding the Turag River in Bangladesh to be considerably polluted by Pb ($1.99 \pm 0.44\text{mg/kg}$) and Cd ($0.84 \pm 0.17\text{mg/kg}$) [96]. The same authors also observed purple amaranth (*Amaranthus lividus*) from agricultural land surrounding the Shitalakhya river in Bangladesh to be polluted by Pb and Cd as well.

Various studies showed that plants grown nearby industrial areas retain more heavy metals and metalloids than those from non-industrial areas (Ahmad *et al.*, 2010; Parvin *et al.*, 2014). Similarly, vegetables grown in high traffic areas were also found to contain higher concentrations of heavy metals and metalloids. Naser *etal.* (2012) found that pumpkin (*Cucurbitamaxima*) grown close to the highway in Joydevpur, Gazipur, contained Pb ($4.76 \pm 1.03\text{mg/kg}$) and Cd ($0.20 \pm 0.02\text{mg/kg}$) in concentrations much higher than those grown in distant areas.

More so, market samples provide important insights into the average contamination levels of heavy metals and metalloids in foods in Bangladesh. Rice, fish, and

vegetables from Kawran Bazar ,Dhaka, were all found to contain Cd and Pb in higher concentrations than these limits (Mih *et al.*, 2017). In their market-based study, Shaheen *et al.* (2016) showed that mangos (*Mangifera indica*) presented excess Pb and tomatoes (*Solanum lycopersicum*) contained excess Cd.

2.6 Health Implications of Heavy Metals Overload in Human Body

Adverse health implications may result from accumulation of heavy metals' overload in human body. The most commonly encountered toxic metals are Arsenic, Lead, Aluminium, Mercury, Cadmium, and Iron. They may enter the body through inhalation, ingestion, or dermal absorption. Exposure to environmental contamination with heavy metal is a growing problem throughout the world that has risen dramatically in the last 50 years as a result of an exponential increase in the use of heavy metal in industrial processes and products. Recently, exposure to heavy metal particles, even at levels below those known to be nontoxic, can have serious health effects (El-Safty, 2014).

Virtually, all aspects of animal and human immune system functions are compromised by heavy metal particulates exposure. The highly reactive nature of most metals results in forming complexes with other compounds such oxygen, sulfide and chloride by which they exert their toxicity (Rusyniak *et al.*, 2010). With ongoing exposure and internal imbalance, the body starts retaining any metals and using them as a substitute for essential elements. For example, lead can substitute calcium, cadmium very readily substitutes zinc, and aluminium may substitute almost all trace elements. Stored heavy metals are locked into the tissues, serving as place holders for the proper nutrients. Heavy metals disrupt a vast array of metabolic processes, alter pro-oxidant/antioxidant balance, and bind to free

sulfhydryl groups, resulting in inhibition of glutathione metabolism, numerous enzymes and hormone function (Mukke and Chinte, 2012).

Nutritionally, heavy metals are directly antagonistic to essential trace elements and compete with nutrient elements for binding sites on transport and storage proteins, metallo-enzymes, and receptors. Disruption of the metabolism and balance of nutrient elements results in marked aberrations in the metabolism of carbohydrate, protein/amino acids, lipids, neurotransmitters, hormones, and increase susceptibility to infections (El-Safty *et al.*, 2009). This can result to damage or reduced mental and central nervous system function by directly influencing neurotransmitter production and utilization. It can lower energy levels through altering numerous metabolic body processes and damage blood composition, liver, kidney, lung, and other vital organs (Hyder *et al.*, 2013).

Concentration of toxic heavy metals can disturb important biochemical processes enhancing oxidative damage which is the key component of chronic inflammatory diseases and initiator of cancer. Mudga *etal.* in 2010 concluded that based on experimental studies that improved the knowledge of human toxicology, heavy metal exposure results in developmental, several types of cancer, kidney damage, endocrine disruption, immunological and neurological disorders. Long-term exposure may result in slowly progressive physical, muscular, and neurological degenerative processes. Heavy metal overload in the adrenal glands reduces the production of hormones, which cause early aging, stress, decreased sex drive and aggravation of menopausal symptoms. It can also lead to unresponsiveness of diabetics to their medications.

In addition, it can lead to neurological diseases such as depression and loss of thinking power. Also aggravate conditions such as osteoporosis and hypothyroidism. For obvious reasons, removing metals from the body safely has been a concern of occupational medicine specialists for many years and recently environmental medicine physicians. In addition, toxic metals can increase allergic reactions, cause genetic mutation, compete with trace metals for biochemical bond sites, and act as antibiotics, killing beneficial bacteria. Much of the damage produced by toxic metals stems from the proliferation of oxidative free radicals they cause. Heavy metals can also increase the acidity of the blood. The body draws calcium from the bones to help restore the proper blood pH (Singh *et al.*, 2011).

Furthermore, toxic metals set up conditions that lead to inflammation in arteries and tissues, causing more calcium to be drawn to the area as a buffer. That contributes to hardening of the artery walls with progressive blockage of the arteries and osteoporosis. The overall vascular effects include oxidative stress, inflammation, thrombosis, vascular smooth muscle dysfunction, endothelial dysfunction, dyslipidemia, immune dysfunction, and mitochondrial dysfunction. The clinical consequences include hypertension, coronary heart disease; myocardial infarction, atherosclerosis, and renal dysfunction with proteinuria. These metallic elements are also classified as human carcinogens (known or probable) according to the US Environmental Protection Agency and the International Agency for Research on Cancer (Houston, 2007).

El-Safty (2014) demonstrated that even minute levels of toxic elements have negative health consequences, affecting nutritional status, metabolic rate, and the integrity of detoxification pathways. For adults, silent symptoms of chronic, low

level heavy metal accumulation in tissues can progress from a steady decline in energy, productivity and quality of life to accelerated cardiovascular disease, premature dementia and total debilitation. Chronic symptoms frequently associated with excessive accumulation of heavy metals include fatigue, musculoskeletal pain, neurological disorders, depression, failing memory, and allergic hypersensitivity. Diagnosing heavy metals overload can be reached through complete medical history, including occupation, hobbies, recreational activities, and environment. An occasional history of ingestion often facilitates the diagnosis, particularly in children.

Nonetheless, physical examination findings will vary according age, sex and health status of the individual, dose or form of the metal present, and time lapse since exposure. Testing for toxic metals in biological fluids such as blood, urine or hair will give a clue for the diagnosis of arsenic, cadmium, lead, and mercury overload. Provocative Challenge tests using 6- or 24-hour urine collection after receiving oral chelating agents may be used to mobilize toxic elements in the body and determining urinary toxic element levels in the collected urine. In addition, hair analysis can be used as a general screening test for the presence of heavy metals. Kidney function should be assessed before starting chelation therapy (Tchounwouet *al.*, 2012).

2.7 Monitoring and Analysis of Heavy Metals in the Environment

Monitoring and analysis of heavy metal concentrations in the environment are necessary for pollution assessment and control (Elzwayiet *al.*, 2017). The levels/concentrations of potentially toxic metals and metalloids should be regularly monitored in the different environmental media such as water, sediments, and soils as well as in the resident biota. Such environmental analysis will provide useful information about distribution, principal sources, and fate of these elements in the environment and their bioaccumulation in the food chains. Such analysis is also used to assess the risk posed by these elements to wildlife and human health as concluded by Ali *et al.* (2019).

2.7.1 Use of Bio indicators and Biomarkers for Assessment of Heavy Metal Pollution

Regarding the use of bio indicators for monitoring and assessment of heavy metal pollution, Morgan (1986) summarizes that “a more meaningful assessment of the impact of metal pollution may be obtained by measuring metal concentrations in selected species of the resident biota.” Different plant and animal species have been used as biological indicators or bio indicators to assess and monitor heavy metal contamination and pollution in the environment. Vongdala *et al.* (2019) opined that different environmental biomarkers can also be used to assess and monitor pollution pertaining to heavy metals in the environment.

2.7.2 The Nature and Scope of Studies on Heavy Metals in the Environment

Environmental studies on different aspects of heavy metals and metalloids are interdisciplinary in nature and require background knowledge in environmental chemistry, eco-toxicology, and ecology. Analysis of xenobiotics such as toxic heavy metals in food chains is an important study area and has environmental, ecological, and economic importance. It has a scope for public health. Such studies involve aquatic chemistry, which has a scope for public health as remarked by Ali and colleagues (2019): “aquatic chemistry is a fundamental element of public health.” Bioaccumulation data of toxic heavy metals in different biota such as fish and rice can be used for health risk assessment for the general human population (Bozhinova, 2016).

2.8 Medicinal Herbs Effective in Treatment of Heavy Metals Poisoning

Key herbs which can act in this way including *Allium sativum* (garlic), *Silybummarianum* (milk thistle), *Coriandrum sativum* (cilantro), *Ginkgo biloba* (gingko), *Curcuma longa* (turmeric), Phytochelatins, triphala, herbal fibers and *Chlorophyta* (green algae) are briefly discussed below:

2.8.1 *Allium sativum*

Allium sativum is an herbal medication containing allin, as its main amino acid. Allin contains sulfur substitutes and in the presence of alliinase is converted to allicin, which then produces other compounds such as: vinyl dithiines, ajoenes, and poly sulfides. Sulfur components are responsible for the smell created by garlic. Allium vegetables, such as garlic, onion, leek and chive, contain organosulfur compounds contributing to clearance of heavy metals such as lead and arsenic by the liver. Also, cruciferous vegetables, such as broccoli, cauliflower, cabbage, kale, Brussels

sprouts, turnips, and kohlrabi are rich sources of sulfur-containing substances (Mehrandish *et al.*, 2019).

2.8.2 Garlic

Garlic has been used as an herbal medication throughout ancient and modern history to prevent and treat a wide range of conditions and diseases. Based on evidences, in the Middle East and East Asia, garlic has been used to treat bronchitis, hypertension, tuberculosis, liver disorders, intestinal worms, rheumatism, diabetes and fever. Garlic is reported to be a wonderful medicinal plant owing to its preventive effects against cardiovascular diseases, lowering blood sugar and cholesterol levels, effective against bacterial, viral, fungal and parasitic infections. Heavy metals can damage the tissues through indirect induction of oxidative stress. It has been shown that garlic has a protective effect on the liver. It has the high effect on poisoning caused by cadmium, mercury and lead, respectively (Nwokocha *et al.*, 2012).

Onion and garlic could be used as an alternative remediation to increase clearance of toxic heavy metals such as arsenic, cadmium, iron, mercury and lead. Garlic is rich in vitamin C, vitamin B6 and manganese. Organosulfur compounds specially and allicin, are biologically active ingredients providing the main protective capabilities of garlic. These components could contribute to detoxification of heavy metals since they are able to bind to most of chemical compounds harboring positive charges. Garlic shows a protective effect against heavy metals poisoning in mice and co-administration of garlic with cadmium or organic mercury for 12 weeks reduces the accumulation of heavy metals in the liver, kidneys, bones and testicles (target organs of cadmium poisoning). Also, it has been shown that regular garlic

consumption reduces the histopathological damages and inhibit serum alkaline phosphatase enzyme (Mehrandish *et al.*, 2019).

Garlic at the higher dosage causes a decrease in mercury accumulation in the brain in animals treated with methyl mercury. This protective effect is because of a smaller amount of mercury absorbed into the brain as a result of the increased excretion of mercury from the body by garlic. The protective effect of garlic is probably caused by sulfur compounds combining with the heavy metals in the body and promoting excretion through bile to the faeces. Studies have also shown that the absorption of garlic through the respiratory tract can limit the effect of lead (Senapati *et al.*, 2001).

2.8.3 Milk Thistle

Milk thistle which is also known as *Silybummarianum* is native to Europe, the Middle East, North Africa, and parts of the Mediterranean region. However, it can be found around the world. Milk thistle history is quite vast. Humans have used milk thistle for more than 2000 years. In ancient Greece the doctors have recommended milk thistle tea as a remedy for snakebites. In the sixteenth century, the English herbalist John Gerard has mentioned milk thistle as an anti-depressant herbal in his “Anatomy of Plants”. In the seventeenth century, physician and herbalist Nicolas Culpeper claimed that milk thistle can help the liver by unblocking it, when the bile ducts blocked, bile builds up in the liver and jaundice developed due to increasing level of bilirubin in the blood, so it also helps to cure jaundice (Chang *et al.*, 2014).

Milk thistle has been used as an herbal medication all over the world. Many of early botanists and pharmacists in ancient Greece and Rome have used milk thistle to aid bile-related problems, which, as we know, are liver-related complications. Also, in traditional Chinese medicine, milk thistle belongs to the category of herbs that clears heat and relieves toxicity. Herbs in this category are used to clear infections, which are referred to as internal heat in traditional Chinese medicine. *Silybummarianum* contains flavonoids such silybin, silychristin, silydianin and 2,3-dehydroderivatives. Oral silybin consumption, especially silybin- β cyclodextrin, protects liver against iron-induced toxicity in mice (Borsari *et al.*, 2001).

Silybin treatment reduces the accumulation of additional malondialdehyde-altered proteins in peritoneal portal hepatocytes (reduces oxidative and lipid proxidative damages). Silybin also reduces liver function impairments. Protective properties of Silybin are possibly explainable by its notable iron binding ability. A group of Italian researches have reported the silybin content for Iron binding (silybin is a component of the silymarin or flavonolignan complex). This complex is found in milk thistle. The study was designed to find an oral and non- synthetic alternative for synthetic iron-binding agent “Desferrioxamine” because this drug has side effects like: bone deformation, sensory impairment and toxicity. These researchers found that silybin bound to ferric iron, strongly even in acidic pH (Borsari *et al.*, 2001).

Regarding its bioavailability silybin seems to have potential to increase the excretion of heavy metals. In addition, the simultaneous consumption of vitamin C (ascorbic acid) and silymarin, results in more improved detoxification of lead by

rats liver. In patients with liver problems arising from toluene and xylene, silymarin could improve liver function (Flora *et al.*, 2010).

2.8.4 Cilantro

Cilantro (*Coriandrum sativum*) is a plant native to Mediterranean region of Europe. Cilantro has been used for at least 5000 years. The cilantro seeds, also known as coriander has been found in ancient Egyptian tomb. Coriander has been used in the treatment of male infertility. The Chinese people have used cilantro for centuries. The ancient Egyptians used coriander tea to treat clinical conditions such as urinary tract infections and headaches. Several studies have been conducted to investigate the potential of cilantro in detoxification of heavy metals. Results of two published studies suggest that this plant could help improve mercury clearance in a number of patients poisoned with heavy metals. However, these studies showed that cilantro established a weaker bond with heavy metals in comparison to allicin of garlic and silybin of milk thistle, indicating that its administration has less priority than garlic and milk thistle(Flora *et al.*, 2010)..

The results of another study showed that cilantro prevented localized placement of lead in mice. However, these results are remarkable for bone tissue and not for soft tissues. In other hand, the relationship between dose and response has not been observed so the presented results are not very reliable (Mudga *et al.*, 2010; Tchounwou *et al.*, 2012).

2.8.5 *Ginkgo biloba*

Ginkgo biloba, known as maidenhair tree, is a plant native to China and has various uses in traditional medicine. *G. biloba* extract is a standard extract of *G. biloba* leaves which exhibits anti-oxidant properties as the free radical scavenger in different organs providing protective benefits against sensory. It is a condition in which the brain has trouble receiving and responding to information that comes through the senses. The results of the study by Tunali-Akbay *et al.* (2007), indicate that lead toxicity causes toxic effects on aorta and the heart which are associated with increased lipid peroxidation and decreased glutathione level.

Ginkgo biloba is one of the herbal remedies useful as a complementary treatment for lead-poisoned patients. *G. biloba* inhibits lead-induced poisoning and corrects the biochemical parameters. Also, *G. biloba* causes the free radicals to be trapped leading to reduced oxidative stress and elevated glutathione level. Increased malondialdehyde production as a consequence of lead poisoning is well-documented. Results of studies show that *G. biloba* consumption significantly suppresses lipid peroxidation and reduces the production of malondialdehyde which is the end product of lipid peroxidation (Tunali-Akbay *et al.*, 2007).

2.8.6 Turmeric

Turmeric is the root of a plant which is scientifically known as *Curcuma longa*. While turmeric is perfectly safe and a wonderful spice, it isn't as useful to our body system as its component, curcumin. Curcumin is a naturally-occurring chemical compound found in the spice turmeric (Mudga *et al.*, 2010). Curcumin is a bright yellow chemical agent produced by some plants. It is a member of ginger family,

Zingiberaceae. Curcumin has been used historically in Ayurvedic medicine against various human diseases. Anti-hepatotoxic effects of curcumin are well-documented and according to the literature, curcumin reduces liver toxicity caused by environmental toxicants such as arsenic, cadmium, chromium, lead and mercury(Mudga *et al.*, 2010).

It prevents histological damage, lipid peroxidation and corrects glutathione level to retrieve the antioxidant capacity of liver and to protect the liver enzymes against oxidative stress. Most of the protective effects attributed to the curcumin arise from its ability to trap free radicals and its chelating property. As indicated in the literature, dietary supplementation could be considered as a natural method for detoxification of heavy metals. Although time-consuming, supplementation with vitamin C, chromium and garlic helps to clear metals from the body, and it does not show the side effects arisen from administration of chemical chelators(Tunali-Akbay *et al.*, 2007).

The study by Hewlings and Kalman highlights two important biological properties of curcumin, one of them is anti-oxidant and the other one is anti-inflammatory effects. According to the results of these researchers, curcumin exerts its antioxidant effect by trapping free radicals and by adjusting the activity of catalase, glutathione and superoxide dismutase enzymes (Hewlings and Kalman, 2017).

2.8.7 Phytochelatins

Phytochelatins are oligomers of glutathione, produced by the enzyme phytochelatin synthase. They are found in plants, fungi, nematodes and all groups of algae. Phytochelatins act as chelators, and are important for heavy metal detoxification.

Phytochelatin composed of three amino acids: glutathione, cysteine, glycine (Glu, Cys, Gly), have been identified in many plant species and in some microorganisms. These compounds are reported to be involved in detoxification of cadmium. Nonetheless, there is little evidence indicating the efficacy of phytochelatin on detoxification of wide range of heavy metals (Vatamaniuk *et al.*, 2001).

In this regard, studies have shown that phytochelatin can form complexes with lead, mercury and silver. The biochemical mechanism underlying detoxification of heavy metals by phytochelatin is very complicated. Briefly, increased concentration of metal ions triggers the activation of the enzyme phytochelatin synthase, then metal ions form complexes with phytochelatin followed by transfer into the vacuoles to form more complexes with sulfide groups and organic acids (Cobbett, 2000).

2.8.8 Triphala

Triphala (*Emblica officinalis*) is a traditional ayurvedic herbal formulation obtained from dried powder of three fruits: Amalaki (known as Bibitaki), *Terminalia bellirica* and haritaki. Triphala has been reported to exhibit anti-bacterial, anti-inflammatory, and anti-diarrheal activities. This traditional formula is able to improve the constipation and regulating the gastrointestinal movements that are important for the removal of heavy metals (Belapurkar *et al.*, 2014).

2.8.9 Herbal Fibres

Herbal fibres play an important role in detoxification of heavy metals. The results of studies show that fibre consumption reduces the exposure to toxins due to increased gastrointestinal motility. Pectin is the most important plant fibre. It is a form of soluble fibre found in many fruits. Consumption of pectin-rich fruits in the diet contributes to improved digestion and owing to its high capability of pectin in binding heavy metals, can support the detoxification process. After ingestion pectin passes directly the stomach and intestine and reaches the colon. As negatively charged compounds, pectin fibres tend to attract the ions of heavy metals. Pectins reach out with their carboxylic groups and grab heavy metals, radionuclides, and bile acids to bind and carry these items out of our bodies, which helps reduce our toxic load (Belapurkar *et al.*, 2014)..

2.8.10 Green Algae

Green algae and some other aquatic plants are capable of absorbing mercury in the environment. It is reported that *Chlorella* in diet increases the clearance of mercury from the digestive tract, muscle, ligaments, connective tissue and bones. *Chlorella* is a green algae which due to its high chlorophyll content acts as a natural chelator of heavy metals, especially lead and mercury. *Chlorella* and cilantro as food materials can detoxify some neurotoxins such as heavy metals (example: mercury) and toxic chemicals (like: phthalates, plasticizers and insecticides) (Uchikawa *et al.*, 2011).

CHAPTER THREE

METHODOLOGY

3.1 Research Settings

Nasarawa state comprises of different categories of solid minerals and the state had 13 Local Government Areas which are subdivided into three senatorial districts: southern senatorial, northern senatorial and western senatorial districts. The southern zone consists of five LGA which are Awe, Doma, Lafia, Keana, and Obi while the Northern senatorial zone consist of only three; they are Akwanga, Nassarawa Eggon, and Wamba while the western zone complete the remaining five, viz Karu, Keffi, Kokona, Nassarawa, and Toto respectively. The most dominant tribes include Hausa/Fulani, Eggon, Alago, Afo and Gwandara (NAGIS, 2015).

This study was conducted in Lafia Local Government Area of Nasarawa State. Lafia is 27.137.8² km in size, it is the capital of Nasarawa State. Nasarawa state is bounded in the North by Kaduna State, in the West by Abuja, the capital city of Nigeria, in the South by Kogi and Benue States and in the East by Taraba and Plateau States (NAGIS. 2015). Located in the savannah region, the lands in Lafia is characterized by a low swampy plain, rugged hill of granite and sandstone, volcanic plugs and plateaus developed on sedimentary and volcanic rock.

Soil and Rivers:- The major soil units of Nasarawa State belong to the categories of Oxisols or tropical ferruginous soil. The soils are derived from the basement complex and old sedimentary rocks; lateritic crust occurs in extensive areas on the plain while hydromorphic soil (humic inceptisols) occurs along the flood plain of major rivers (Akwa *et al.*, 2007). Major urban centres particularly Lafia and Keffi

are heavily gullied, since most of the inhabitants of the state are farmers, extensive areas in the countryside are also cleared for farming, thus exposing wide areas and land to sheet erosion.

In Lafia, the soil can be classified into four broad zones, these are: the wawa soil type, the mixed farming soil, black cotton soil type, the mixed farming soil type which covers the western half of the Shabu district, the whole of Agyaragu district, part of Adogi district and a small section of areas around Tudun Adabu district. The soil covers half of the area and it has deceptive appearance of fertility, but its porosity amount to very low moisture. Since the soil covers a large chunk of the land area, one would appreciate the reason for the predominance of livestock rearing and the cultivation of cotton, beniseed (Redi in Hausa), peanut and cereals. The Benue Rivers also play an important role in the socio-economic and political life of the area. The mixed farming soil type is a belt approximately in kilometres wide running down the Eastern edge of the wawa type soil.

Vegetation, Flora, Fauna and Edible Vegetables:-The vegetation type include stunted shrubs and stumpy trees of sixteen to twenty feet high, mostly of tropical forest types. The area been open grassland does not have much forest reserve land. Few notable ones include Kanawa forest and other strategic location mainly artificial created by the Agricultural Development Projects. But then unfortunately, the natural environment- the flora, the fauna, important birds and wild life have declined and are on the verge of total extinction in Lafia.

As expected, the vegetation and ecology of Lafia has been adversely affected by excessive cultivation, bush burning, deforestation (cutting down of trees for firewoods), mining activities, population increase, construction of roads, bridges

and houses, the creation of small scale industries, etc (Akwa *et al.*, 2007). Common edible vegetables within the study area include; fluted pumpkin leaves (*Telfairia occidentalis*), African spinach "Green" (*Amaranthus hybridus*), Pawpaw (*Carica papaya*), water leaf (*Talinum triangulare*), etc.

Geology and Relief:-The Southern landscape of the state forms part of the low plains of Benue origin. Other parts of the state are composed of undulating lowlands and a network of hills developed on granite, migmatite, pegmatites and gneisses. Around the salt mining villages of Awe are a number of worn volcanic cones. The state is drained by numerous fast flowing streams/rivers that take their source from the Jos plateau and flowing into the River Benue which also mark the state Southern boundary prominent among these are the Mada, Dep, Ayini and Farin Ruwa Rivers.

Climatic Conditions:- Nasarawa State like other parts of the country is characterized by a tropical sub humid climate with two distinct seasons: the wet season and the dry season. The wet season starts from about the beginning of May and ends in October, while the dry season is experienced between November and April. Annual rainfall figures ranges from 1100mm to about 2000mm; about 90% of the rain fall between May and September, with the wettest months being July and August. The rain normally comes in thunderstorm of high intensity particularly at the beginning and at the end of the raining season. Temperatures are generally high during the day particularly between months of March and April. The mean monthly temperatures in the state ranged between 20°C and 34°C, with the hottest month being March and April and coolest months being December and January.

Mineral Deposits:- Just as its slogan simply “home of solid minerals”. Lafia local government area is totally proud of solid minerals and agro based raw materials in large quantities such as uranium, tantalite, columbite, silica, barile, emerald, granite, gemstone, iron ore, limestone and others too many to mention (Akwa *et al.*, 2007).

3.2 Sample Size Determination and Sampling Techniques

Four (4) political wards, two (2) each from urban and rural areas of Lafia were assessed. Twenty eight (28) people were recruited at random per ward making a total of one hundred and twelve (112). Thus 112 questionnaires were distributed to the study candidates in order to identify the probable route of exposure and the impact of heavy metal contamination of the environment on their health and general wellbeing.

Due to large size of the target population, the researcher used the Taro Yamani formula to arrive at the sample population of the study.

$$n = \frac{N}{1+N(e)^2}$$

Where:

N is the approximate population of inhabitants in proximity to the sampling sites.

1 is the constant (in this case, the constant was represented by the number of wards assessed which is **4**)

e is the degree of error expected

n is the sample size

$$n = \frac{120}{4+120(0.05)^2}$$

$$\frac{120}{4+120(0.0025)}$$

$$\frac{120}{4+0.36}$$

$$\frac{120}{4.36}$$

$$n = 27.5$$

$$n = 28$$

3.3 Sampling Sites

The sampling sites were selected based on their proximity to areas of anthropogenic activities and human settlement. Such activities include mining, agro-allied, pharmaceutical, small scale farming, animal rearing, fishing activities, rock breaking, clothes washing and swimming.

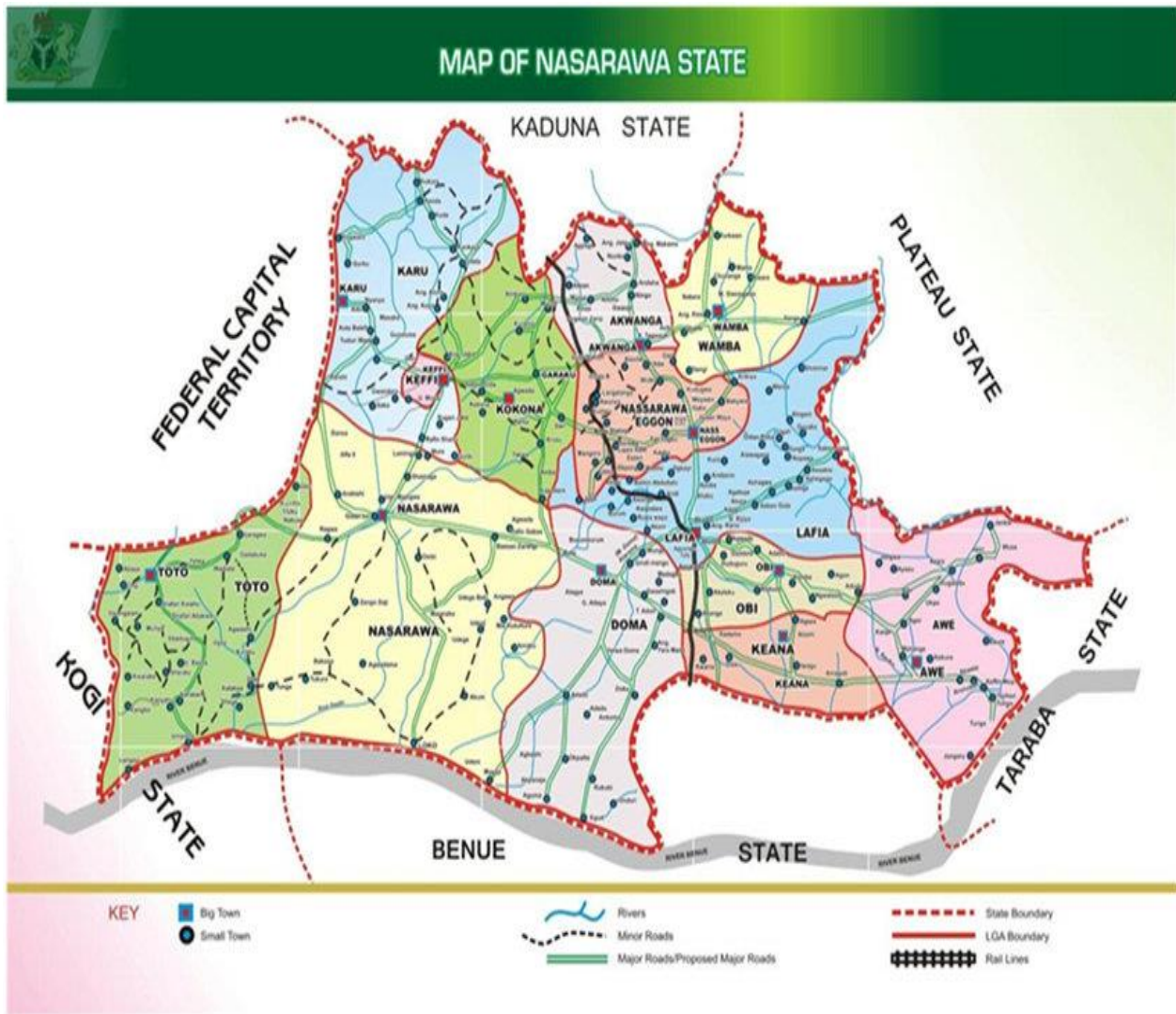


Figure 3.1: Map of Nasarawa State Showing the Study Area

3.4 Sample Collection and Processing

3.4.1 Soil Sample

A total of ten (10) topsoil sites were sampled. The method of Huang *et al.* (2019) was used for collection of soil sample. At each sample site, four sub samples were collected from an approximately 16m² grid and thoroughly mixed to achieve a total composite soil sample weight of about one-kilogram. The soil samples were then sealed in plastic bags and air-dried at room temperature (20–25°C) for further analysis. After which the samples were filtered through a 2mm and a 2µm polyethylene sieve in sequence, plant roots and shredded rocks were removed from the soil sample to prepare for chemical analysis.

3.4.2 Water Sample

The technique of Vongdala *et al.* (2019) was adopted for collection of water samples. A total of ten (10) samples from surface water inland fill wetlands, from an average water depth of 1–1.5m were collected each from four different areas within the two wards in Lafia from upstream to downstream. Good quality samples were randomly taken from each of the sampling site, and another two subsamples were obtained accordingly. The samples were later stored in 1-L polyethylene bottles and subsequently adjusted by HNO₃ to obtain pH<2. The values of pH, temperature (°C), electrical conductivity (EC), and dissolved oxygen (DO) were measured using a U-50 Multi parameter Water Quality Meter within the sampling sites. Furthermore, two groundwater samples were collected from wells inside and in the vicinity of mining area, farm land which agrochemicals had been used on, and wetlands where animals are reared.

3.4.3 Edible Vegetables

A total of 4 (four) different edible vegetable samples were collected in two ponds within the sampling sites at Lafia. The samples were collected in both wet and dry seasons. The roots, stems, and leaves of the plants obtained were separated and stored in zipped polyethylene bags. Thereafter, the samples were washed thoroughly with tap water and rinsed with distilled water for 1 minute to clear them of periphyton and detritus as recommended by Gworek *et al.* (2016). The vegetation samples were then dried at 40°C for 2 days in an oven until a consistent weight is maintained, after which the samples were grounded into a fine powder by a mortar and stored in the dark at 5°C for further analysis as described by Vongdala *et al.* (2019).

3.5 Chemical Analyses of Heavy Metals

3.5.1 Analysis of Water Samples

The surface and ground water samples were filtered by filter papers to obtain a 100-mL solution, to which 1 mL of HNO₃ (65%) was added and then heated for 2 hours without boiling at 80–90°C. The samples were then cooled to room temperature and then filtered again with 0.2-µm syringe filters as demonstrated by (Kar *et al.*, 2008). The water samples were then analyzed using a multi type Inductively Coupled Plasma Emission Spectrometer (ICP-ES) and ICPE-9000.

3.5.2 Analysis of Soil Samples

The method of Vongdala *et al.* (2019) was used for heavy metals determination in the soil samples. Briefly, five (5) grams of soil was added to 20mL of HNO₃ (7 mol/L), stirred for 1 hour, and then placed in an autoclave at 120°C for 30 min. The mixtures were then cooled to room temperature, filtered by filter papers, and diluted

by deionized water. The samples were then filtered again by a 0.2- μ m syringe filter and transferred to tubes for analyses by ICPE-9000.

3.5.3 Analysis of Edible Vegetable Samples

Heavy metal determination of roots, stems, and leaves of edible plant samples was conducted by initially drying and grounding these plants parts into powder form. Thereafter, 0.5g of each sample was added to 6mL of concentrated HNO₃ (65%) and 2mL of concentrated HCl (30%) and allowed to stand until the reaction is completed. The mixture was then moved to an autoclave for 66 minutes at 132°C for digestion as described by Andersen and Kissler (2004). The plant samples were further analyzed by ICPE-900.

3.6 Ecological Risk Assessment of Heavy Metals

3.6.1 Pollution Load Index (PLI)

Pollution load index (PLI) represents the number of times by which the metal content in the sample exceeds the background concentration. It provides comprehensive information about the metal toxicity in a particular sample (Yang *et al.*, 2011). The pollution load index (PLI) is defined as the *n*th root of the multiplications of the concentrations; i.e., the square roots of the calculated pollution index. The PLI value of >1 indicates polluted, whereas <1 indicates no pollution (Barakat *et al.*, 2012). PLI was evaluated using the following formula proposed by Tomilson *et al.* (1980).

$$PLI = (CF_1 \times CF_2 \times CF_3 \cdots \times CF_n)^{1/n}$$

Where n is the number of metals identified and CF is the contamination factor. The contamination factor can be calculated from the following relation:

$$CF = \frac{\text{Metal concentration in sample}}{\text{Background value of metal}}$$

According to Håkanson (1980), $CF < 1$ indicates low degree of contamination, $1 < CF < 3$ indicates moderate degree of contamination, $3 < CF < 6$ indicates considerable degree of contamination, and $CF > 6$ indicates very high degree of contamination.

3.6.2 Contamination Degree (CD)

This parameter refers to the sum of all contamination factors. It gives an indication of the degree of overall contamination in sediments from a sampling site. It expressed as:

$$CD = \sum_{i=1}^n CF_i$$

Håkanson (1980) proposed the classification $Cd < 6$ is low degree of contamination, $6 \leq Cd < 12$ is indicative of moderate degree of contamination, $12 \leq Cd < 24$ indicates considerable degree of contamination, and $Cd \geq 24$ represents very high degree of contamination.

3.6.3 Potential Ecological Risk Index (RI)

The potential ecological risk could be used to evaluate the ecological risk of heavy metals in sediments by considering the toxicity of the metal and a comparison between the concentration of the metal and the background value. RI was used in this study to quantify the potential ecological hazard of contaminated samples. Håkanson (1980) provides a formula to estimate RI.

Firstly,

$$E_r^i = T_r^i \times CF,$$

Where T_r^i is the toxic response factor for a given substance and CF is the contamination factor.

The toxic response factor assigned to the following heavy metals Co, Cd, Cu, Zn, Mn, Pb, and Ni to be used in the calculation of potential ecological risk index (RI) are 5, 30, 5, 1, 1, 5, and 5, respectively as previously adopted by Jiao *et al.* (2015) and Soliman *et al.* (2015).

3.6.4 Soil-Plant Transfer Coefficient (%)

The soil-transfer coefficient was calculated as ratio of a heavy metal in a plant (dry weight) to a total heavy metal concentration in the soil as shown in the following equation as demonstrated by Kacholi and Sahu (2018):

$$TC = \frac{C_{\text{plant}}}{C_{\text{soil}}} \times 100$$

TC is transfer coefficient (%), C_{plant} is heavy metal concentration in vegetable tissue (mg/100g), and C_{soil} is metal concentration in soil (mg/100g dry soil).

3.7 Human Health Risk Assessment of Heavy Metals

3.7.1 Exposure Assessment

Exposure to toxic heavy metals could also be of significant concern to humans living close to contaminated environment. In this present study, three primary pathways of exposure to heavy metals when dealing with human health risk assessment were considered. They are ingestion, dermal contact, and inhalation. The exposures through ingestion, inhalation, and dermal contact were calculated respectively using equations proposed by Enuneku *et al.* (2018):

$$1) \text{ EXP (ingestion)} = \frac{\mathbf{C} \times \mathbf{IRs} \times \mathbf{ED} \times \mathbf{EF}}{\mathbf{BW} \times \mathbf{AT}}$$

$$2) \text{ EXP (dermal)} = \frac{\mathbf{C} \times \mathbf{CF} \times \mathbf{SA} \times \mathbf{AF} \times \mathbf{ABS} \times \mathbf{EF} \times \mathbf{ED}}{\mathbf{BW} \times \mathbf{AT}}$$

$$3) \text{ EXP (inhalation)} = \frac{\mathbf{C} \times \mathbf{IR(inh)} \times \mathbf{EF} \times \mathbf{ED}}{\mathbf{PEF} \times \mathbf{BW} \times \mathbf{AT}}$$

Where **C** is the concentration of heavy metals in the samples, **IRs** is the ingestion rate (114mg/day); **CF** is the unit conversion factor (10⁻⁶kg/mg); **EF** is the exposure frequency (350days/year); **ED** is the exposure duration (30years); **BW** is the body weight (70kg); **SA** is the exposed skin surface area (5700 cm²); **AF** is the adherence factor from sediment to skin (0.07mg/cm²); and **ABS** is the dermal absorption from sediment (0.001) (unitless); **SL** is the skin adherence factor (0.2 mg cm⁻² h⁻¹) for children and (0.2 mg cm⁻² h⁻¹) for adults; **PEF** is the particle emission factor (1.316 × 10⁻⁹m³ kg⁻¹); **AT** is the average time. For non-carcinogens, it is **ED** × 365days. For carcinogens, it is 70 × 365 = 25,550days.

Similarly, dietary intake of contaminated food has been implicated as a primary source of human exposure to toxic chemicals including heavy metals. The exposure

through ingestion of contaminated edible plants (vegetables) was calculated using equation below:

$$\mathbf{EXP(diet)} = \frac{\mathbf{C} \times \mathbf{IR(biota)} \times \mathbf{ED} \times \mathbf{EF}}{\mathbf{BW} \times \mathbf{AT}}$$

Where **C** is the concentration per mass of the medium (ppm), **IR** is the ingestion rate of the medium (g/day), **ED** is the exposure duration (years), **EF** is the exposure frequency (days/year), **BW** is the body weight (kg) and **AT** is the average time (years).

3.7.2 Public Health Risk Characterization

3.7.2.1 Assessment of Hazards to Human Health

The potential non-cancer risk of heavy metal concentrations in the sampling sites was characterized using a hazard quotient (HQ). Hazard quotient (HQ) assumes that there is a level of exposure known as the reference dose (RfD). It is estimated that a daily oral intake of the heavy metal at the reference dose will pose no reasonable risk even to sensitive populations, over a 70-year lifetime (Afrifa *et al.*, 2013). USEPA (2010), defines hazard quotient (HQ) as the ratio of the average daily intake or dose (ADD) (mg/(kg/day)) to the reference dose (RfD, mg/(kg/day)). It was estimated using the formula:

$$\mathbf{HQ} = \frac{\mathbf{EXP}}{\mathbf{RfD}}$$

Where **HQ** = hazard quotient (unitless), **ADD** = average daily dose (mg/kg-day), **RfD** = Reference dose (mg/kg-day). For n number of heavy metals, the non-carcinogenic effect to the population is as a result of the summation of all the HQs due to individual heavy metals.

$$HI = HQ_1 + HQ_2 \dots + HQ_n$$

If the HI is less than 1.0, it is highly unlikely that significant additive or toxic interactions would occur, so no further evaluation is necessary. When the HI exceeds 1.0, there may be a concern for potential non-cancer health effect.

3.8 Statistical Analysis

Data obtained from this study were analysed using the Statistical Package for Social Sciences (SPSS) IBM version 22 software. Both descriptive and inferential statistical analysis were carried out and used thereafter to describe the data obtained in the study. One-way Analysis of Variance (ANOVA) was conducted to test differences among measured parameters with respect to sampling locations. Statistical significance was set at $P \leq 0.05$.

3.9 Ethical Issues

Ethical clearance and authorization for the study was sought from the Lafia Local Government Health Department, while permission to assess sampling sites was obtained from the owners of the mining sites, the farmers in case of farmlands and other people undertaking any anthropogenic activities within any of the sampling sites. Likewise an informed consent was obtained from the participants that volunteered to participate in the study and the screening was done at no cost whatsoever to them. All information obtained from this study was handled confidentially.

CHAPTER FOUR

RESULTS

Table 4.1: Heavy Metals Detected from Soil Samples within Lafia and Environs, Nasarawa State

Heavy Metals	Sampling Location			
	Shabu	Agyaragu	Adogi	Tudun Adabu
Cd	+	+	+	+
Cu	+	+	+	+
Zn	–	+	–	+
Mn	+	+	+	+
Pb	–	+	+	–
Fe	+	+	+	+
Ni	+	+	+	+

Key: + = Present, – = Absent

Assessment of heavy metals from the different soil types showed that Cd is present in the soil of Shabu, Agyaragu, Adogi and Tudun Adabu. Cu was also detected from the soil types of the four locations sampled. Zn on the other hand is present in the soil samples of Agyaragu and Tudun Adabu, but absent in the soils of Shabu and Adogi accordingly. Mn, Fe and Ni were also detected from the soil samples of the four locations within Lafia, Local Government Area of Nasarawa State. Nonetheless, Pb was detected in the soils of Agyaragu and Adogi, but absent in the soils of Shabu and Tudun Adabu (Table 4.1).

Table 4.2: Heavy Metals Detected from Water Samples within Lafia and Environs, Nasarawa State

Heavy Metals	Sampling Location			
	Shabu	Agyaragu	Adogi	Tudun Adabu

Cd	+	+	+	+
Cu	+	+	+	+
Zn	+	+	+	+
Mn	+	+	+	+
Pb	–	+	+	+
Fe	+	+	+	+
Ni	+	+	–	+

Key: + = Present, – = Absent

The detection of heavy metals from water samples within Lafia Metropolis and environs was reported in Table 4.2. Cd was found to be present in all the four locations sampled viz: Shabu, Agyaragu, Adogi and Tudun Adabu. In the same vein, Zn, Mn and Fe was also detected in all the water samples from the four sampling locations assessed; while Pb was detected in the water samples of all areas sampled with the Shabu. Similarly, Ni was observed to contaminate water samples from Shabu, Agyaragu and Tudun Adabu, but was obviously absent in the water samples of Adogi.

Table 4.3: Heavy Metals Detected from Edible Vegetable Samples within Lafia and Environs, Nasarawa State

Edible Vegetables				Heavy Metals		
Cd	Cu	Zn	Mn	Pb	Fe	Ni

Fluted pumpkin leaves (<i>Telfairiaoccidentalis</i>)	+	+	+	+	-	+	+
Green African spinach (<i>Amaranthushybridus</i>)	+	+	+	+	+	+	+
Water Leaf (<i>Talinumtriangulare</i>)	+	+	+	+	+	+	+
Jute Leaves (<i>Corchorus sp</i>)	+	+	+	+	+	+	+
Control sample-	-	+	-	-	-	-	-

Key: + = Present, - = Absent

*Control Sample = uncontaminated vegetable samples collected from the demonstration farms of the Nasarawa State College of Agriculture Lafia

Heavy metals contamination of the edible vegetables assessed was presented in Table 4.3. Cd, Cu, Zn, Mn, Fe and Ni were found to be present in *T. occidentalis*, *A. hybridus*, *T. trangularare* and *Corchorus* spp. However, Pb was detected in three of the four edible vegetables screened except from fluted pumpkin leaves. Nonetheless, all heavy metals with the exception of Zn were completely not detected from the control vegetable samples collected from the Nasarawa State College of Agriculture Lafia.

Table 4.4: Calculated Contamination Degree and Pollution Load Index (PLI) of Soil, Water and Edible Vegetable Samples from Lafia and Environs, Nasarawa State

Heavy Metals	Soil	Water	Vegetable	Total Samples
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Cd	1.84	1.86	1.88	1.86
Cu	0.46	0.15	0.20	0.27
Zn	2.86	1.57	1.91	2.11
Mn	0.62	0.26	0.28	0.38
Pb	0.08	0.02	0.04	0.05
Fe	174.93	45.95	97.17	106.02
Ni	0.32	0.09	0.19	0.20
PLI	1.19	0.47	0.67	0.78

Contamination degree and pollution load index of the soil, water and edible vegetables showed that the soil samples were more contaminated with heavy metals followed by vegetables and lastly water. The contamination degree of the soil samples was highest for Fe at 174.93mg/kg, followed by Zn (2.86mg/kg) and Pb has the lowest contamination degree of 0.08mg/kg. Meanwhile, the contamination degree of water samples was within the ranges of 0.02–45.95mg/kg, while that of the edible vegetable samples ranged between 0.04–97.17mg/kg. However, the mean contamination degree of the three environmental samples against all the heavy metals detected was highest for Fe (106.02) and Zn (2.11), but lowest degree was observed for Pb (0.05). The pollution load index was highest for soil (1.19kg/ml), followed by vegetable (0.67mg/kg) and lastly water (0.47mg/ml) (Table 4.4).

Table 4.5: Individual Potential Risks and Potential Ecological Risks Index of Soil, Water and Edible Vegetable Samples from Lafia and Environs, Nasarawa State

Heavy Metals	Soil	Water	Vegetable	Total Samples
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Cd	55.11	55.7	56.44	55.78
Cu	2.32	0.76	1.01	1.36
Zn	14.30	7.87	9.54	10.57
Mn	0.64	0.20	0.29	0.38
Pb	3.08	1.28	1.39	1.92
Fe	14.30	7.87	9.54	10.57
Ni	1.60	0.47	0.96	1.01
RI	77.11	66.39	69.67	71.06

Individual potential risks and potential ecological risks index of soil, water and edible vegetable samples in Lafia and environs was presented in Table 4.5. Potential risk in soil, water and edible vegetable was highest in Cd: 55.11, 55.78 and 56.44, but lowest in Mn: 0.64, 0.20 and 0.29 respectively. However, the Risk Index of 77.11 for soil samples was the highest, followed by 69.67 for edible vegetable samples and lastly 66.39 for water samples accordingly.

Table 4.6: Exposure Concentration of Heavy Metals (ppm) in Soil and Water Samples within Lafia Metropolis and Environs, Nasarawa State

Heavy Metals	Environmental Samples	
	Soil (mg/kg) ± S.D	Water (mg/ml) ± S.D
Cd	0.73 ± 0.46	1.00 ± 0.64
Cu	5.46 ± 1.386	2.42 ± 10.21
Zn	79.47 ± 12.54	132.67 ± 23.55
Mn	22.50 ± 3.69	51.41 ± 7.32
Pb	2.85 ± 0.63	5.62 ± 0.87
Fe	98.90 ± 12.29	233.31 ± 25.01
Ni	3.08 ± 1.48	8.49 ± 2.54

Key: S.D. = Standard Deviation

The concentration of exposure of the heavy metals for both the soil and water samples showed that Fe with a concentration (ppm) of 98.90 ± 12.29 was the most occurring contaminant in the soil followed by Zn (79.47 ± 12.54) and Mn (22.50 ± 3.69); while for water samples, Fe, Zn and Cu with an exposure concentration (ppm) of 233.31 ± 25.01 , 132.67 ± 23.55 and 62.42 ± 10.21 were the most encountered (Table 4.6). However, Cd is the lowest concentration in terms of exposure for soil samples (0.73 ± 0.46 ppm) and also for water samples (1.00 ± 0.64 ppm).

Table 4.7: Estimated Daily Intake (EDI) of Heavy Metals (mg/kg) amongst the Study Population from Consumption of Vegetables

Edible Vegetables	Heavy Metals						
	Cd	Cu	Zn	Mn	Pb	Fe	Ni
Fluted pumpkin leaves (<i>Telfairiaoccidentalis</i>)	0.001	0.011	0.021	0.007	0.001	0.023	0.014
Green African spinach (<i>Amaranthushybridus</i>)	0.002	0.009	0.018	0.008	0.001	0.017	0.012
Water Leaf (<i>Talinumtriangulare</i>)	0.004	0.034	0.022	0.006	0.002	0.015	0.009
Jute Leaves (<i>Corchorus</i> sp)	0.002	0.007	0.015	0.0011	0.004	0.021	0.008

Estimated Daily Intake (EDI) of heavy metals from ingestion of edible vegetables in Lafia Local Government Area of Nasarawa State was presented in Table 4.7. Accordingly, *T. occidentalis* has Fe (0.023) and Zn (0.021) as the most ingested heavy metals by the inhabitants of the study areas. Similarly, Zn and Fe had an EDI (mg/kg) of 0.018 and 0.017 respectively for *A. hybridus*. On the other hand, *T. triangulare* had an EDI of 0.034 ppm and 0.022 ppm for Cu and Zn respectively. The highest estimated daily intake of heavy metals for jute leaves (*Corchorus* sp.) showed highest concentration for Fe (0.021ppm) and Zn (0.015ppm).

Table 4.8: Specific Hazard Index (HI) for Inhabitants Exposed to Contaminated Environmental Samples from Lafia and Environs, Nasarawa State

Heavy Metals	Soil	Water	Vegetable	Hazard Index
Cd	0.353	0.296	0.006	0.655
Cu	1.661	0.775	0.006	2.442
Zn	3.487	0.801	0.005	4.293
Mn	1.353	0.384	0.006	1.743
Pb	0.04	0.37	0.008	0.418
Fe	2.924	1.364	0.01	4.298
Ni	1.204	0.693	0.015	1.912

Hazard Index (HI) for the inhabitants exposed to the heavy metal contaminants from environmental samples of Lafia was presented in Table 4.8. The specific hazard posed by the heavy metals within the soil environment ranged between 0.04–3.487, while those of the water samples ranged from 0.296–1.364, while the vegetable samples was within the range of 0.005–0.01. The actual hazard index however was highest for Fe (4.298) and Zn (4.293), while the lowest HI was recorded for Pb (0.418).

Table 4.9: Soil-Vegetable Transfer Coefficients (%) of Heavy Metals from Different Parts of Lafia and Environs, Nasarawa State

Edible Vegetables	Cd	Cu	Zn	Mn	Pb	Fe	Ni	Efficacy
<i>T. occidentalis</i>	0.15	5.82	2.88	1.42	1.08	0.49	2.14	1.99
<i>A. hybridus</i>	0.11	5.48	1.87	0.89	0.61	0.38	1.32	1.52
<i>T. triangulare</i>	0.04	3.84	0.86	1.12	0.15	0.17	0.92	1.01
<i>Corchorus</i> sp.	0.20	3.07	3.35	0.96	0.14	0.20	0.85	1.25
Average	0.13	4.55	2.24	1.09	0.49	0.31	1.31	1.44
USEPA Guideline (μgL^{-1})	5.0	1300	500	50	15	300	-	-

The soil-vegetable transfer coefficients of the heavy metals indicates that Cu with values of 5.82%, 5.48% and 3.84% has the highest transfer coefficients in *T. occidentalis*, *A. hybridus* and *T. triangulare* respectively. However, for *Corchorus* sp., Zn (3.35%) showed the highest transfer coefficient. The average transfer coefficient of the heavy metals on the edible vegetables screened was 4.55% for Cu, 2.24% for Zn, 1.31% for Ni, 1.09% for Mn, 0.49% for Pb, 0.31% for Fe and 0.13% for Cd. More so, the efficacy of transfer of the heavy metals on the vegetables was highest in *T. occidentalis* (1.99%), *A. hybridus* (1.52%), *Corchorus* sp. (1.25%) and *T. triangulare* (1.01%); while the average efficacy of transfer of the heavy metals was 1.44% as presented in Table 4.9.

CHAPTER FIVE

DISCUSSION, CONCLUSION AND RECOMMENDATIONS

5.1 Discussion

In this present study, Cd, Cu, Mn, Fe and Ni was detected in the soils of all the locations sampled. Zn and Pb were observed to be present in 2 and 3 of the 4 areas assessed. The same trend was also observed for both water and vegetable samples within Lafia Local Government. This scenario is expected since the locations where samples were collected are in proximity to mining locations and other areas of human anthropogenic activities. The presence of heavy metals in the environmental samples particularly in water is quite worrisome because it was observed from literatures that heavy metals are extremely toxic to aquatic organisms even at very low concentrations (Ahmed *et al.*, 2014). These elements can cause significant histopathological alterations in tissues of aquatic organisms (Afrin *et al.*, 2015). The concentrations of copper recorded in soils were below the WHO/FAO (2007) permissible limit of 100 mg/kg. The values recorded were within the normal range of copper concentration required by plants for growth and development.

More so, the concentration of copper recorded in this study was lower than earlier reported values of 47.0mg/kg reported by Fisseha *et al.* (2008) and 22.14 mg/kg around an oil depot at Jos in Nigeria (Babatunde *et al.*, 2014). Additionally, the concentrations of lead in soils were below the WHO/FAO (2007) permissible limit of 50mg/kg. However, substantial amount of lead concentration was recorded at the study area indicating some anthropogenic source of lead pollution in the environment. The values recorded in this study were higher than of 14.13mg/kg and 13.53mg/kg recorded in a previous study by Babatunde *et al.* (2014). Similarly, the zinc content of soils analyzed was below the WHO/FAO (2007) permissible limit

of 300mg/kg. However, the values of zinc recorded in this study were within the normal range of zinc required by plants. The concentration of zinc observed in this study was lower than 237.96mg/kg reported in an earlier study (Okunola *et al.*, 2007).

The aquatic habitat on the other hand are contaminated by heavy metals from different sources, however, Zhuang *et al.* (2013) confirmed that one major source of heavy metals in the aquatic ecosystem is effluents from mining operations. Nasarawa State in general is known for large-scale mining activities, this perhaps explains the presence of 7 heavy metals in soil, water and edible vegetables of Lafia. On the basis of mean contamination degree of the heavy metals on the environmental samples analysed, Fe (106.02) had the highest contamination degree, while Ni (0.20) had the least contamination degree. The Pollution Load Index exceeded 1.00mg/kg for soil samples (1.19). The results depicted soil samples in Lafia to be heavily contaminated with heavy metals suggesting possible anthropogenic impacts. This corresponds with an earlier report by Fosu-Mensah *et al.* (2018) and Enuneku *et al.* (2018).

More so, the individual potential ecological risks of the heavy metals depicted the highest mean potential risk for Cd, Zn and Fe, while the Risk Index was higher in soil samples (77.11) compared to edible vegetables (69.67) and water (66.39). The potential risk index for the heavy metals is significantly high. In fact, they were higher than those observed by DeForest *et al.* (2007), Enuneku *et al.* (2014) and Enuneku *et al.* (2018). It is important to note however that Pb has a comparably low individual potential risk index compared to the other heavy metal. This perhaps could be due to the category of solid minerals mined within the vicinity of the

sampling locations. Lead is not mined per say in Lafia but could be introduced into the environment through other human anthropogenic activities other than mining. Several workers such as Duruibe *et al.* (2007), Dzoma *et al.* (2010), Khan *et al.* (2011) and Kamunda *et al.* (2016) reiterate this particular assertion, which conform to the findings of this present study.

Accordingly, exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing young and infants being more sensitive than adults (NSC, 2009). Lead poisoning, which is so severe as to cause evident illness, is now very rare. Lead performs no known essential function in the human body; it can merely do harm after uptake from food, air, or water (Raymond and Felix, 2011; Musa *et al.*, 2017). Despite the complexity, the toxicity of heavy metals in plants and in animals and humans that eat contaminated plants is primarily associated with previous environmental contamination (Tasrina *et al.*, 2015). Therefore, the presence of lead in the environmental components of Lafia even though minimal is a threat to public health.

Interestingly, the soil-vegetable transfer coefficients observed for this particular study were greater than 1 for Cu, Zn, Mn and Ni. The standard of the United States Environmental Protection Agency (USEPA) stipulates that transfer factor of >1 transfer factor of heavy metals for foods including cereals and vegetables is deleterious. Ibadon *et al.* (2014) opined that a transfer factor of 1 and above indicates that the metal is biomagnified. Except for Pb and Cd, all other transfer factors in *T. occidentalis*, *A. hybridus*, *T. triangulare* and *Corchorus* sp. were above 1 indicating that there was bio-magnification of the rest heavy metals in the edible

vegetables of Lafia. The soil-to-plant transfer of heavy metals is a very important step in the trophic transfer of such metals in food chains. These metals are taken up by plants from polluted soil and subsequently transferred to herbivorous animals along the food chain as demonstrated by Nica *et al.* (2012).

In fact, those workers pointed out regarding the contamination of the human food chain, that contamination of crops such as cereals and vegetables is a very serious issue. In this present study, almost all the heavy metals detected had significant soil-to-plant transfer coefficient. Orisakwe and colleagues (2012) in their work on the risk of consuming heavy metal contaminated food in Owerri Nigeria deduced that the consumption of foods contaminated with toxic heavy metals may cause risk to human health. On the same note, heavy metals in higher concentration ranges have been reported in vegetables grown with wastewaters compared to those grown with groundwater. Furthermore, higher concentrations of these metals have been found in leafy vegetables compared to those in other types of vegetables such as bulbs and tubers as reported by Mahmood and Malik (2014). This reinforced the findings of this present study.

5.2 Conclusion

In this study, seven heavy metals namely: cadmium, copper, zinc, manganese, lead, iron and nickel were found at varying concentrations in soil, water and edible vegetables within Lafia metropolis and environs. The mean concentrations of most of the heavy metals in the soil samples were found to be within their natural corresponding background values, while the pollution load index of the soil is high, but those of water and edible vegetables were not too high. The PLI reported in this research can provide a valuable information and advice for policy and decision makers to evaluate the pollution status of Lafia in Particular and Nasarawa State in general. Hence, subsequent investigation should be conducted intermittently to monitor environmental pollution due to the on-going mining activities and evaluate the public health risks associated with metal pollution on miners and inhabitants of such areas.

5.3 Recommendations

From the findings of this study, the following recommendations became necessary:

- a) The industries operating in this community should adopt more sustainable and eco-innovative management options in order to attenuate potential ecological and human health risk of metal pollution.
- b) Remediation methods should be adopted by the Nasarawa State Waste Management Board and other local authorities to safeguard the general health of communities living close to areas of human anthropogenic activities..

- c) It is vital that the bioaccumulation values rather than the total contents of heavy metals should be taken into consideration during risk assessment henceforth for proper evaluation of human health risk of the contaminants.

- d) It is vital to monitor extensively and occasionally heavy metals in vegetables especially those grown in areas with close proximity to mining locations or those irrigated with water of poor chemical and biological quality in order to safeguard the health of the population.

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